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JOURNAL OF THE AIR POLLUTION CONTROL ASSOCIATION

Founded 1907

Vol. 5, No. 4
February 1956

How Meteorology Affects Air Pollution

(See page 235)

STACKS

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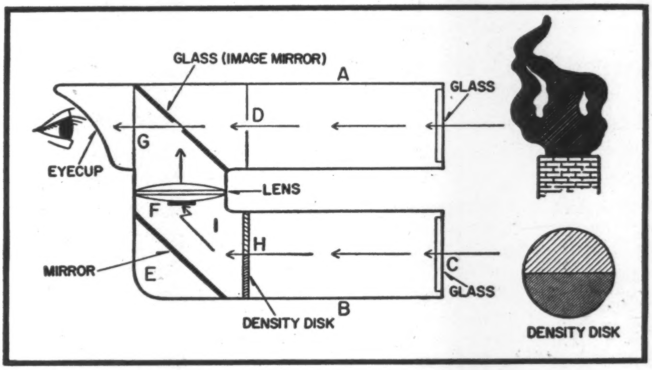

- ***How it works*—Smoke picture fills field of vision through apertures C, D, and G. Light from area adjacent to stack is transmitted through reference disc, H, in barrel, B, to surface of mirror, E. Image of reference disc projects through lens, F, to image mirror where it is compared with smoke seen through apertures. Center of reference disc is blocked by opaque disc, I.**

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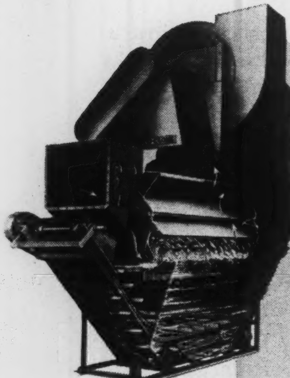

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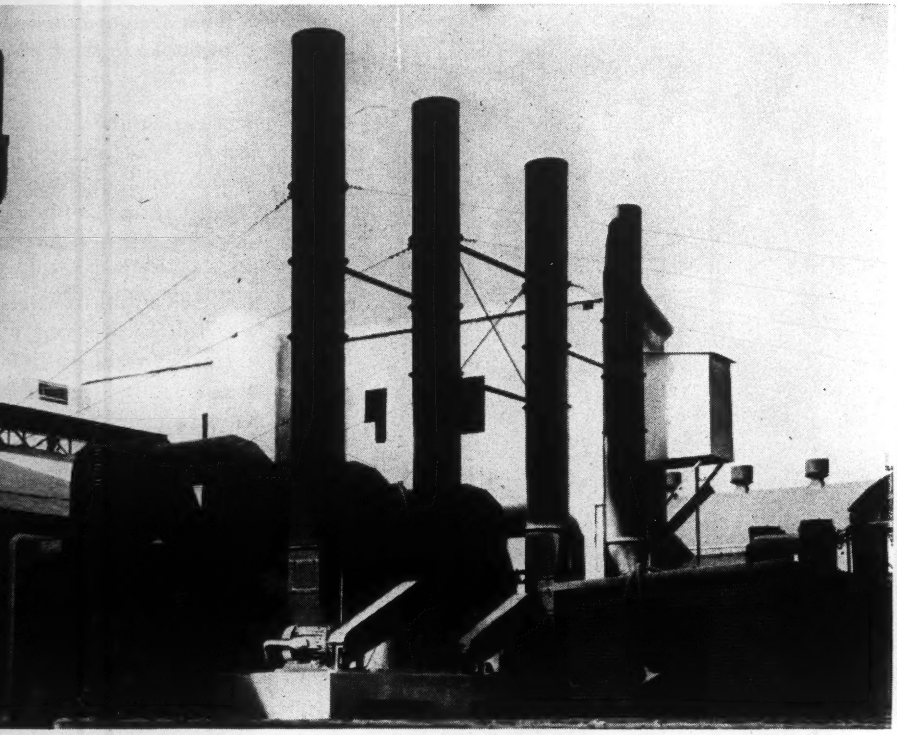

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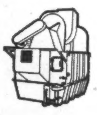

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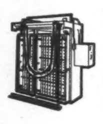

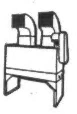

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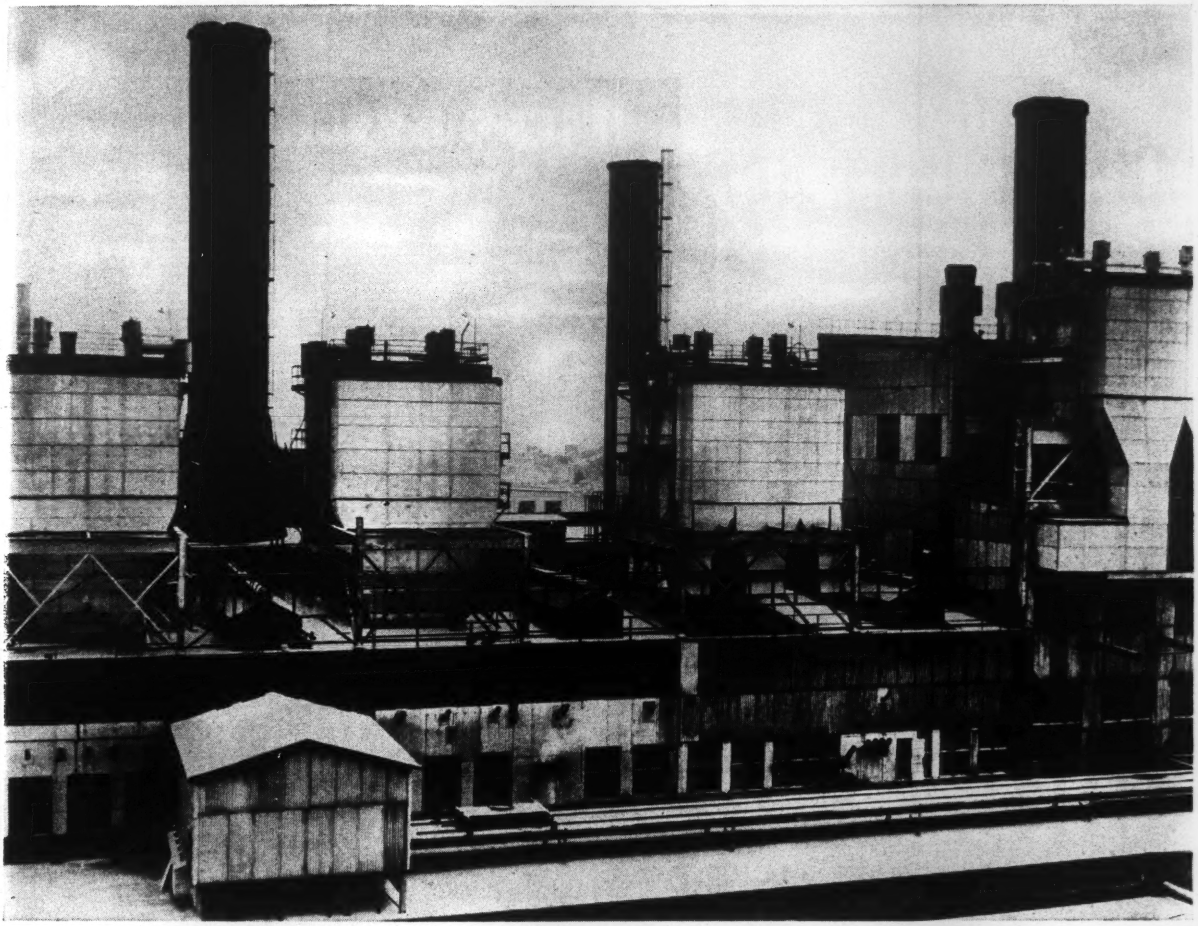

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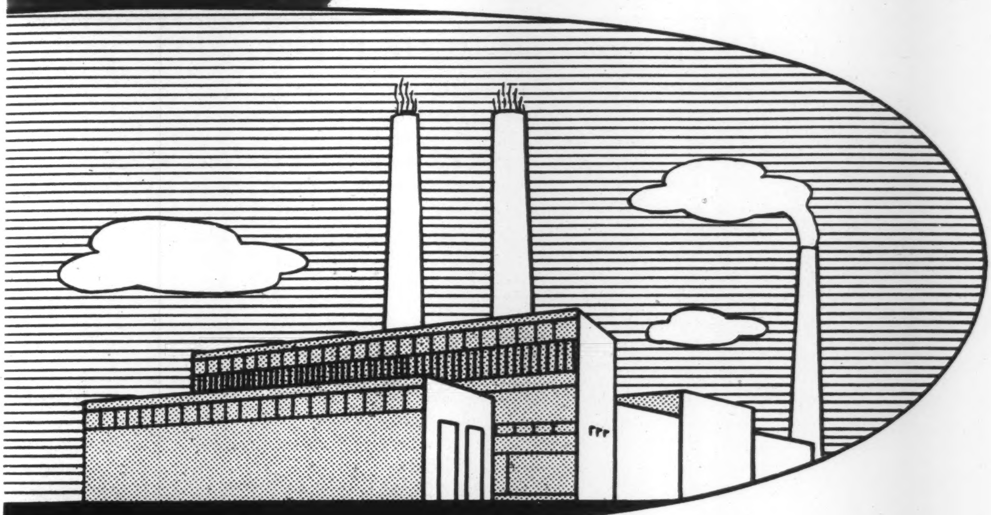

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(*Formerly "Air Repair"*)

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The Editor welcomes writers interested in air pollution problems and encourages them to use the pages of this journal for the expression of their opinions. But neither he nor the Association assumes responsibility for the validity of the opinions expressed herein.

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Adaptation of Titrilog for Field Mobile Sampling

S. B. CARPENTER and R. E. SPARKMAN

Division of Health and Safety
Tennessee Valley Authority
Wilson Dam, Alabama

The air pollution studies program carried on by TVA has been briefly described elsewhere by Thomas[1]. An important part of these studies is the collection and analysis of data on atmospheric diffusion of SO_2 in the stack gases. In studying the diffusion of SO_2 in the stack gases, TVA conducts a program of mobile field sampling to supplement the data collected from fixed (Thomas SO_2 autometers) installations.

Much effort and time have been devoted to the development and use of special SO_2 sampling equipment. Scrubbers were first utilized in this work which provided only a value for average concentrations over the period of sampling. It became apparent that more information on the variations in concentration or absence of SO_2 in the atmosphere during a part of the sampling period was desirable. To get this information a conductimetric SO_2 sampler and analyzer was constructed from a design furnished by M. D. Thomas to operate from an automobile utilizing vacuum from the intake manifold for sample collection; and also a Thomas autometer was mounted in a trailer and attempts made to sample downwind.

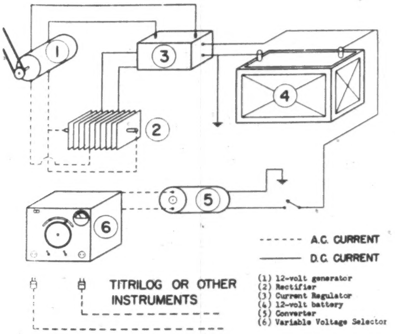
None of these devices fully met field sampling requirements. Scrubbers employing a small hand-operated vacuum pump essentially limited the sample period to 10 min., provided only an average value of the concentration, and required a cumbersome field titration. The conductimetric SO_2 analyzer employing automobile manifold vacuum eliminated the manual feature of sampling. It also provided average concentration, but values could be determined for short intervals up to 2 min. by referring resistance readings to a calibration scale. However, this type of record was not considered to satisfactorily reflect the fumigation patterns. While the Thomas SO_2 autometer is a very satisfactory instrument for stationary or semi-fixed operation, it was not operated successfully as a fully-mobile instrument. Problems were encountered with the provision of satisfactory gasoline-generated power, with time required for stabilization and limitations due to its bulk. Mounting in a separate trailer limited desirable travel over unimproved roads. This problem would have been lessened but not eliminated by mounting in a properly-insulated small truck.

A portable model Titrilog, a recently-advanced automatic instrument for continuous sampling and recording of SO_2 and other pollutants, was later acquired to replace the improvised portable SO_2 sampling equipment. To use the Titrilog successfully in a mobile field sampling program, a number of modifications were necessary to adapt it for use in a car or helicopter. With these modifications or adaptations it is our experience that the portable Titrilog is currently the best available instrument for field study of dispersion of certain gaseous pollutants. While a team of 2 individuals may offer some advantage, it can be operated quite successfully by one person, who also drives the automobile. A description of these modifications may be helpful to others having an interest in similar studies.

Operation of Titrilog in Car

The layout of the electrical system for the operation of the Titrilog and recorder in an automobile is shown in Fig. 1a. To meet the required power capacity the electrical system of the automobile should be converted to a 12-v. system. The regular 6-v. DC generator is replaced by a 12-v. AC generator and rectifier which delivers 12 v. of DC current to the regulator and battery circuit. Due to the heavy load that the generator is required to carry, a heavy-duty belt made for the particular generator should be used. Power to the instrument is supplied by a 12-v. DC-AC converter which operates off of the automobile's 12-v. heavy-duty storage battery and supplies 115 v. AC. The voltage is manually regulated between 115 and 120 v. by a variable voltage transformer. With this arrangement the instrument can be operated at correct voltage although the car motor is running at idling speed. Fig. 2 shows the general instrument location as used in the automobile. The Titrilog is mounted on sponge rubber in the back seat. The recorder and all controls are in the front seat. A very good record can be obtained with the car moving at slow speeds. When sampling in hot weather at a fixed point for 30 min. or more, raising of the hood will prevent over-heating of the car.

One-fourth-inch stainless steel and tygon tubing is used for the sample in-


1
3
4
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D.C. CURRENT
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(1) 12-volt generator
(2) Rectifier
(3) Current Regulator
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(5) Converter
(6) Variable Voltage Selector

Fig. 1a. Automobile electrical layout

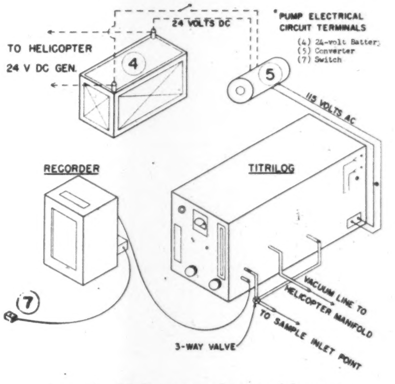
TO HELICOPTER
24 V DC GEN.
24 VOLTS DC
4
5
*PUMP ELECTRICAL CIRCUIT TERMINALS
(4) 24-volt Battery
(5) Converter
(7) Switch
115 VOLTS AC
RECORDER
TITRILOG
7
VACUUM LINE TO HELICOPTER MANIFOLD
TO SAMPLE INLET POINT
3-WAY VALVE

Fig. 1b. Helicopter electrical layout

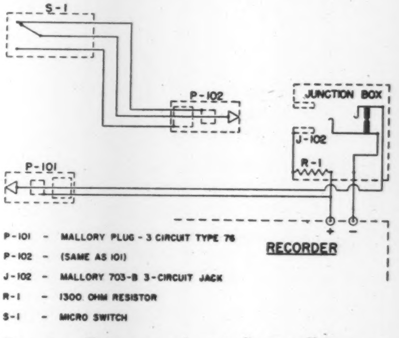
S-1
P-102
JUNCTION BOX
J-102
R-1
P-101
+
−
RECORDER
P-101 - MALLORY PLUG - 3 CIRCUIT TYPE 76
P-102 - (SAME AS 101)
J-102 - MALLORY 703-B 3-CIRCUIT JACK
R-1 - 1300 OHM RESISTOR
S-1 - MICRO SWITCH

Fig. 1c. Diagram of switch installation on recorder

---

[1] Thomas, Fred W., "TVA Air Pollution Studies Program," *Air Repair* 4, 2, 7-12+ (1954).

Fig. 2. Instrument location as used in the car

take line which should be located on the opposite side from the car exhaust and should extend 6 to 12 in. above the car top. For best results when sampling, the car exhaust should be on the downwind side from the source of sample. When not in operation, especially in hot weather, the suction line should be broken at the reagent cell to prevent backflow and contamination of the sample lines.

Operation of Titrilog in Helicopter

Aerial Sampling By Helicopter

A method for study of dispersion patterns as described elsewhere by Gartrell and Carpenter[2] has been employed by TVA very successfully as a means of measuring SO_2 concentrations in the plume. Some trouble was encountered at the beginning of operation but was later resolved and the necessary modifications and adjustments made. Fig. 1b shows the layout of the electrical system used on the helicopter to operate the amplifier and recorder. Fig. 3 illustrates the installation of the Titrilog in a helicopter. This system requires only the installation of a 24-v. DC-AC converter which operates off of the helicopter 24-v. battery and generator. To minimize drain on the electrical system, the air pump on the Titrilog was disconnected. Vacuum was provided by connecting a 1/4-in. rubber hose from the intake manifold on the helicopter engine to the Titrilog. Due to space limitations it was not possible to use the zero box in the helicopter to provide for the zeroing of the instrument. To overcome this limitation, a 3-way valve was inserted in the sample intake line, conveniently located, so that the pilot could connect the filter into the line for zeroing the instrument while in flight. A special ink pot consisting of a very small lightweight cup welded on the forward side of the pen was used to prevent air pockets from forming in the pen and stopping it from inking while in flight. Fig. 1c shows the diagram of a switch installed on the recorder for marking time-ticks on the recorder chart to indicate the starting and ending time of a sample run. This permits the distinction between samples where several runs are made on the same flight.

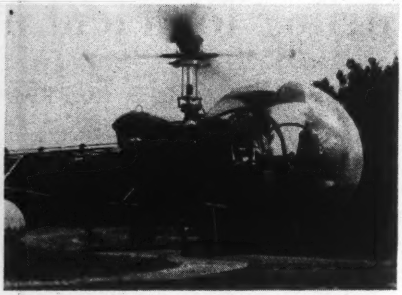

Fig. 3. Instrument location as used in the helicopter

Calibration of Cell

Due to intermittent operation and conditions under which the Titrilog is operated, it was found necessary for more accurate results to calibrate the cell at approximately weekly intervals. The use of pure SO_2 gas was found to be very economical and satisfactory for calibration where a laboratory is available. The following equipment and supplies are required:

1. One lb. cylinder of SO_2 with needle valve
2. Vacuum cleaner which will supply from 15 to 20 cfm. of air
3. Flowrater, with range from 2 to 26 cfm. from metering airflow
4. One set of 5 variable (low flowrates) flowmeters for measuring SO_2 gas and sample
5. Twelve-gal. glass jug for mixing chamber
6. Tygon and rubber tubing for making necessary connections

Shown in Fig. 4 is the layout and arrangement of this equipment. The most accurate results using SO_2 gas were obtained when following the procedures listed below:

1. A constant flow of at least 15 cfm. of air together with a minimum flow of 8 cc./min. of SO_2 gas should be supplied to the mixing chamber (jug) for sample makeup.
2. Both air and SO_2 outlets should extend approximately half way down into the jug, the lines being placed side by side with the SO_2 line extending approximately 1 1/2 in. below the air outlet.
3. The air flow to chamber should always be started before SO_2 gas.

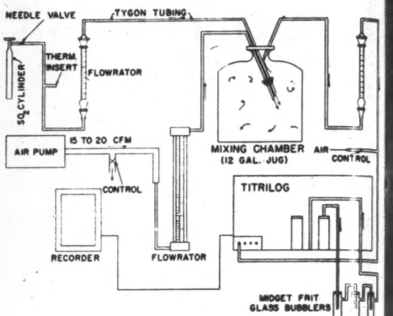

Fig. 4. Layout and arrangement of calibration equipment using SO_2 gas

4. Both air and SO_2 gas to mixing chamber should be allowed to flow some 2 to 3 min., or until the flow is leveled off before taking sample.
5. Sample intake for instrument should be near the mouth of the jug.
6. The air intake for dilution of sample to instrument should be taken from the outside or through a filter to avoid any SO_2 that might escape to room.
7. Sufficient air should be mixed with sample flow from jug to obtain net titration level between 30 and 50.
8. The sample should be allowed to run until curve on chart levels off.
9. Sample line to instrument should be cleaned (lines that have been used for pure SO_2 gas will give false readings).
10. An occasional chemical analysis should be made of sample gas for ppm. of SO_2 to check against volume calculations of SO_2.
11. All calibrations with SO_2 gas should be made in the laboratory with the mixing chamber under the hood to avoid SO_2 fumes.

Summary

This article describes methods for installation and operation of the Titrilog in an automobile and a helicopter for mobile field sampling for SO_2. Frequent calibration is required and a method for calibration of the Titrilog using SO_2 is also described.

Acknowledgment

The author gratefully acknowledges the helpful suggestions and assistance of Joseph G. Hobson, Transportation Branch, Division of Property and Supply, who planned and installed the modified electrical system; and of John W. Moffett, Maintenance Branch, Division of Chemical Operations, who helped develop the modified ink pot.

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[2] Gartrell, F. E., and Carpenter, S. B., "Aerial Sampling by Helicopter: A Method for Study of Diffusion Patterns," J. Meteorology, 12, 3, 215-19 (1955).

Domestic Gas-Fired Incinerators*

F. E. VANDAVEER
The East Ohio Gas Company
Cleveland, Ohio

Domestic gas-fired incinerators have been on the market for more than 25 years, but their potential value was not recognized until about 1950. With the introduction of the low gas input or dehydrator type of incinerator, and improvements in the fast-burning intermittent units, distribution in our area, for example, began increasing from a total of 1,861 in 1950, to 7,783 in 1951, 17,010 in 1952, so that as of January 1, 1955, there were over 65,600 incinerators in the Cleveland area. There are about 85,000 incinerators in all cities served by The East Ohio Gas Company. Similar experiences were recorded in Detroit where 90,000 domestic incinerators have been installed, as well as in a number of other cities to varying degrees. National sales in 1954 were over 100,000 incinerators. The potential market appears to be very great. There are now 37 manufacturers of incinerators with 115 models approved by the American Gas Association. Ten years ago there were only 3 or 4 manufacturers of a few models.

With the mounting cost of collecting and disposing of garbage, the difficulty of finding locations for new municipal incinerators, or nearby places to dump and cover garbage, city officials began studying the possibilities of the domestic gas incinerator several years ago. A few cities made it mandatory that an incinerator or a garbage grinder, or both, be installed in all new homes. At least one large city investigated the possibility of purchasing and supplying incinerators to all residences. Air pollution officials and city authorities have become interested in the possible affect of these units, and incinerators in general, on purity of the city air. In most locations, the reaction has been favorable, or one of watchful waiting and encouragement of manufacturers and utilities to make further improvements. A few officials in cities with unusual atmospheric conditions have discouraged the use of incinerators.

It might be expected during a pioneering and development stage on domestic incinerators that there would be some misunderstanding of what present day units will do or will not do and what improvements are contemplated for the future. Having inspected and tested many of the incinerators on the market, having participated in A.G.A. approval requirements committee activities to strengthen test requirements, having served as chairman to date of the A.G.A. research committee on incinerators, and having participated in various city committee discussions on this subject, possibly we are in a position to clarify some of these questions.

As a basis for this discussion, the American Gas Association's definition of a domestic gas-fired incinerator will be used. It is an appliance which is sold and installed as a packaged, completely assembled, direct fed, free standing unit limited to not more than 5 ft.^{3} capacity and a burning rate of 25 lb./hr. of Type 1 (dry combustibles) and Type 2 (50% dry combustible and 50% food refuse) wastes. A few types and sizes of incinerators now on the market are illustrated in Fig. 1. Domestic incinerators are not designed for commercial or industrial use, they are not intended for burning large volumes or all kinds of combustible wastes, they are not backyard trash burners, and they are not dependent on paper or other dry combustibles for incineration of food refuse.

Contemporary Incinerators

Early in the incinerator program several things were done in Cleveland which contributed to better construction of the appliance and more satisfactory installations. These included:

1. Preparation and printing of a booklet on Recommended Practices for Installation of Domestic Gas-Fired Incinerators on the East Ohio Gas Company System. These booklets were issued to dealers, installers, and manufacturers, and to our service men.
2. Models of all incinerators merchandized in our area were obtained for thorough inspection and tests in our laboratories. A typical arrangement of test equipment is shown in Fig. 2. A number of improvements were made in several incinerators as a result of this work.
3. In the City of Cleveland permits from the building department for incinerator installations were required.
4. Only those incinerators approved by the City of Cleveland Board of Building Standards and Appeals may be installed in the city. American Gas Association approval is usually accepted by the Board. Approval is being granted on a 6 months' time basis, after which renewal of approval is necessary. At these intervals the Board requests reports of progress on strengthening A.G.A. requirements and on incinerator research, as well as reports from the building department and from the Air Pollution Commissioner. Some members of the Board have witnessed performance demonstrations of incinerators

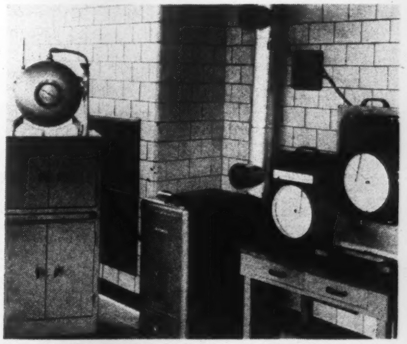

Fig. 2. Arrangement of equipment for testing a gas-fired incinerator. L. to r. a wet test gas meter, the incinerator connected by vent pipe including 2 automatic draft controls to a chimney, a flue gas draft pressure recorder and a temperature recorder.

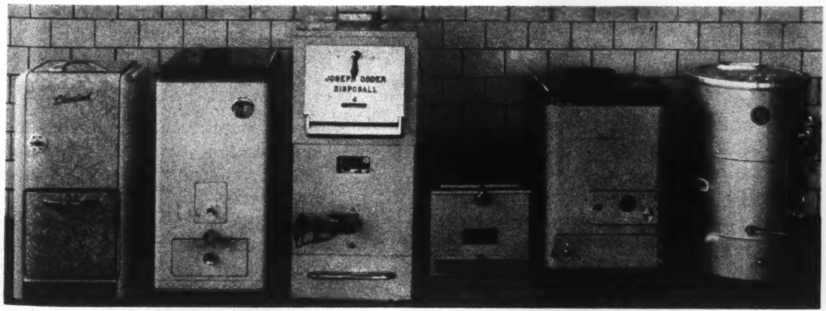

Fig. 1. Representative types and sizes of contemporary domestic gas-fired incinerators. Sizes shown vary from a .67 to 3 bu. capacity and gas inputs from 2,000 to 38,000 Btu./hr.

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*Presented at the 48th Annual Meeting of the Air Pollution Control Association at Detroit, Mich., May 22-26, 1955.

at our laboratories.

Our field experiences with incinerators may be summarized briefly:

1. During a test period of 4 weeks in November and December, 1954, during which all complaints on incinerators were inspected, our company received no complaints of smoke or odor from incinerators.
2. Service requests for adjustments or repair on incinerators are very low.
3. The Air Pollution Department of the City of Cleveland has referred no complaints of smoke or odor to us which were attributable to domestic gas-fired incinerators.
4. A survey of 66 incinerator installations and interviews with 72 neighbors by our men in December, 1953, disclosed the following results:
    a. Four installations were producing an odor. This was caused by improper charging of the incinerator and failure to shake the grates and remove ashes. This condition was corrected and no complaints have been received since that time.
    b. A few incinerators were producing a thin, white smoke.
    c. Fly ash was reported in one instance which was found to be caused by a non-fuel-fired unapproved incinerator.
    d. All owners were satisfied with their incinerators and neighbors were not complaining.
5. No complaints of smoke or odor have been received from a housing project where incinerators are installed in each of 250 houses.
6. Gas consumption based on tests with sub-meters in employees' houses varied from 900 to 2,000 ft.^{3}/mo. depending upon size of family, and averaged 1,250 ft.^{3} of natural gas/mo. This would amount to an average monthly gas cost of 75 cents. These values would apply to either low gas input or high input incinerators.

As a result of these tests, inspections, and field experiences, it is our feeling that contemporary domestic gas-fired incinerators should be acceptable to air pollution control officials for the following major reasons:

1. In the burning of garbage and paper mixture for which incinerators are designed, only a thin, white smoke is generated. An attempt to get a picture of this smoke is illustrated in Fig. 3 at the time of taking a sample for counting number and size of fly ash particles. No smoke is shown, but there was some visible to our observers. There appear to be no generally accepted standards for regulating white smoke emissions, and instruments for satisfactorily measuring it have not been perfected. Recent tests with a Bacharach True-Spot Smoke Tester indicate the possibility of adapting it for testing of incinerator flue gases. The oil burner smoke scale graduated from 0 as pure white to 9 as black with 8 gradations from white to black in between these 2 numbers may be adaptable. During test with a definite charge, such as the new A.G.A. mixture, a time limit for smoke generation at some selected number and the remainder of the time at number 3 or lighter might be considered as a possible test method.
2. From 3 to 4½ lb. of paper and garbage/day will be thrown away by an average family of 4. It can be calculated that such a mixture may produce 16 ft.^{3} of CO_2, 70 ft.^{3} of air and nitrogen and a variable amount of water vapor in the flue gases for each pound of mixture. Three pounds would produce 258 ft.^{3} of flue gases and 4½ lbs. would yield 387 ft.^{3} of flue gases. About half of this weight of coal (1½—2¼ lbs.) would produce the above listed volumes of flue gases.
3. Normally, 3 to 4½ lb. charges of waste material are burned in ½ to 1 hour's time/day. Smoke would be visible about ½ of this time for a total of not more than 1.0 to 2.1% of the day.
4. A domestic incinerator will produce less flue gases per day than a domestic coal or coke furnace, or an oil furnace, or less than an automobile; and an incinerator in every house in town would produce less smoke and fly ash than the coal-fired electric generating station for that town.
5. The odor of burning paper and cooking or burning food refuse persists for a much shorter period of time and in far less volume than the thin, white smoke as a general rule. At infrequent intervals a smoldering action producing objectionable odors in small volume may occur on low gas input incinerators.
6. Fly ash from incinerators is not a problem. Very few particles larger than smoke are discharged from a chimney and these are observed only for a few minutes a day during very rapid burning of the mixture. On one of the low input incinerators tested using the A.G.A. charge of garbage and paper the largest particle trapped in the Bausch and Lomb dust counter was 13 μ, but there were a few larger particles.
7. New American Gas Association approval requirements completed within the past 2 yr. and others under preparation to become effective at an early date will insure more satisfactory operating incinerators. The Air Pollution Control Association is represented on this committee by Harry C. Ballman. These new requirements include:
    a. Limiting updraft during tests to .01 in. (It was formerly .03 in).
    b. A new test charge of garbage and paper simulating household waste consisting of 40% by weight of dry combustible (cardboard, newspaper, waxpaper) and 60% food refuse (potatoes, cabbage, oranges, bread, rice, beef suet, water) has been established. The former test charge was beet pulp, suet, starch, and water wrapped in 2½ lb. packages with newspapers.
    c. A barometric draft control or equivalent will be required.
    d. Operating and installation instructions are required.
    e. No emission of smoke or odor into the room will be allowed.
    f. Ash drawer capacity has been increased to the equivalent of 20% of the garbage compartment. (It was 10%).
    g. A test requirement limitation and a method of test for smoke and odor from the chimney is being prepared.
8. Domestic gas-fired incinerators are much better than back yard trash burners and fuel-less incinerators and should not be confused with them because:

(continued on page 242)

Fig. 3. A thin white smoke visible to observers but not caught in the picture was issuing from the chimney to which a contemporary incinerator was connected and was burning a mixture of paper and garbage. A sample of the flue gases is being taken in a Bausch and Lomb dust counter.

Survey of Gas-Fired Domestic Incinerators[*]

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Early in 1953 a certain city decided to eliminate garbage collection, most of the rubbish collection, and at the same time dispose of these wastes by use of gas-fired domestic incinerators. The City Council was influenced in its decision by the fact that land area was at a premium and not available for use of the land fill method of disposal. Furthermore, municipal incinerators were considered to be costly, and also involved land area. Collection problems still remained with either land fill or municipal incineration. The use of domestic incinerators seemed like a panacea for the troubles of City Council since, if incineration could be carried out in the home, many problems would be solved and considerable savings to the city would result. Therefore, the City Council decided to install an incinerator in each of the homes at city expense, the cost of operation to be borne by the homeowners. The initial cost was to be balanced against savings which would result.

The author directed the tests to determine the suitability of domestic gas-fired incinerators for the purpose intended. In all, 14 incinerators were tested. It is the writer's opinion that these are representative of the units produced in the United States.

General Purpose

The purpose of the investigation was to study 14 domestic gas-fired incinerators and to determine the characteristics of each as they affect suitability for installation in the homes concerned.

After considerable study it was decided to expand the general purpose of the investigation to accomplish the following:

(a) Evaluate operational safety in terms of:
  (1) Stack temperatures
  (2) Wall temperatures
  (3) Floor temperatures
  (4) Incinerator surface temperatures
  (5) Temperatures of handles, etc.
  (6) Hazards
(b) Evaluate the relative garbage burning capacity of each unit in terms of:
  (1) Time required for disposition of the charge
  (2) Nuisances, including smoke, fly ash, odors, and condensible vapors
  (3) Cost of operation
(c) Evaluate the efficiency of garbage burning in terms of Btu. supplied/lb. of standard garbage load.
(d) Observe effects of operation as evidenced by:
  (1) Failure of parts or components
  (2) Failure of refractories, insulation, etc.
  (3) Failure of surface finish, including discoloration, cracking, etc.

Description of Equipment

Test Booth

The test booth specified by the American Gas Association was adopted with minor modifications. The booth actually used is described as follows:

The back and side wall shall be vertical at right angles, 6 ft. in height, of 1-in. thick boards and finished in flat black. The floor shall be of 1-in. tongue and groove oak flooring finished in clear varnish.

Thermocouples embedded flush in floor and walls were used for temperature determination. The thermocouples were of No. 24 AWG copper constantan, the wires being soldered $\frac{1}{8}$ in. apart in 0.352 in. diam. copper discs, 0.022 in. thick.

Floor thermocouples were spaced 6 in. x 6 in. Wall thermocouples were installed in movable "probes" (boards carrying 18 thermocouples spaced 3 in. x 3 in.) By using the movable probes, temperatures could be measured at any desired location in the wall or incinerator surface without the necessity for installing permanently a much larger number of thermocouples. In addition, the probes allowed for considerable flexibility in operation.

Carbon Dioxide Analysis

Since it became obvious that the test runs would involve considerable time and would necessarily be continuous, it was decided to adapt a carbon dioxide analyzer to a recorder and obtain a continuous CO_2 chart.

For simplicity and dependability in continuous operation, it was decided to utilize the principle of differential thermal conductivity in the analysis. The instrument chosen was calibrated against dry room air as a reference standard. The flue gas was sampled continuously and dried before it entered the instrument.

The instrument's indication was proportional to the volumetric concentration of a product of combustion in the flue gases. The analyzer as used to activate a recording potentiometer.

By utilizing the differential thermal conductivity principle, it was possible to determine completeness of combustion, since carbon dioxide percentage increases in the flue gas with complete combustion of the wastes.

Smoke Determination

Smoke samples were obtained by use of a filter type smoke indicator which shows the smoke density as a function of the density of a spot produced by filtration of a standard volume of stack gases. The spot density on the filter is interpreted by means of a standard scale which indicates maximum permissible smoke density for common types of smoke producing equipment.

Stack and Blower Installation

A metal stack about 60 ft. in height and 12 in. in diam. was used in these tests. An induced draft fan was connected into the stack so that controlled draft conditions could be maintained. A barometric damper was used to finally control the draft and keep it constant at 0.03 in. of water. Draft was measured by a standard inclined draft gage.

Wall and Floor Temperatures

Twenty selected thermocouples were used in a special switching circuit to provide a temperature profile of the test booth. The record was made by a recording potentiometer. The chart speed was increased to provide reasonable time increments for the purpose intended, which was to read temperatures at each of the 56 thermocouples involved.

The thermocouple switching circuit was designed around a 20 position telephone type stepping relay. A pair of synchronous timing motors was the basis of the switching circuit. A one revolution/hour motor fired a circuit which started the telephone relay in operation. At 20 sec. intervals the second motor closed a switch which advanced the telephone relay one step. A limiting circuit turned the switching circuit off after 20 readings had been taken. At the start of the next hour the 1 RPH. motor turned the circuit back on. This provided for 1 reading at each of 20 points in each hour although all readings were accomplished within 5 min. out of the hour.

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[*] Presented at the 48th Annual Meeting of the Air Pollution Control Association at Detroit, Michigan, May 23-26, 1955.

Stack Temperatures

Stack temperatures were determined by means of Armored Iron Constantan thermocouples installed in the vertical flue leading from the incinerator. The thermocouples were placed approximately 6 ft. from the top of the incinerator.

General Procedure

After considerable study and investigation it was decided that the standard test loads developed by A. G. A. were reasonable and well suited to this investigation.

The burning was done in 2 separate tests. One test was made with shredded newspaper to determine the following items:

(a) Stack temperatures
(b) Wall temperatures
(c) Floor temperatures
(d) Smoke
(e) Odors
(f) Fly Ash
(g) Effects on incinerator
(h) General observations

Another test on simulated garbage was made to determine the following items:

(a) Fuel consumption
(b) Stack Temperatures
(c) Wall temperatures
(d) Floor temperatures
(e) Smoke
(f) Odors
(g) General observation

The firing procedures established by A. G. A. were followed for the Hot Load (shredded newspaper).

The general firing procedures specified by A. G. A. were followed for the simulated garbage load with the exception that the quantity of load was reduced to ½ of rated capacity. It is the author's contention that this smaller load was favorable to the incinerator.

All temperatures were measured by use of thermocouples and checked with a calibrated potentiometer and mercury-in-glass thermometers, except as indicated.

Relative smoke density was determined by use of a smoke gage.

Fuel consumption was measured with the wet-type gas meter.

The problem of odor measurements was thoroughly investigated, and it was decided that the research involved in determining a method of measuring odors quantitatively was prohibitive and not within the scope of this investigation. This project would require an estimated 2 yr. of basic research and expenses well beyond the maximum possible here. A similar conclusion was reached concerning emission of condensible vapors. Therefore, it was decided to observe as carefully as possible the actual conditions of operation and form opinions based on observations.

Procedure

The incinerator under test was examined for physical characteristics, installed in the booth in such a position that the side was 12 in. from the side thermocouple probe surface, and the rear of the flue riser was 18 in. from the rear thermocouple probe surface. Necessary connections to gas supply and stack were made. The manufacturer's specified rate of gas supply was established and checked against the wet gas meter. Then a test was run on shredded newspaper. Following this another test was run on a simulated garbage load. Below is a description of these test procedures.

Shredded Newspaper Charge

At 6 min. intervals, 7 suitable-sized charges of shredded newspaper were loaded into the incinerator chamber and burned to heat the incinerator and surroundings. After the 7th load, the process was continued until all stack, floor and wall temperatures had been recorded by the equipment previously described.

Simulated Garbage Load

After 15 to 30 min. of burner operation to permit determination of the percentage of CO_2 due to the burner only, a test charge, mixed and wrapped as hereafter described, was loaded into the incinerator chamber, with attention to the positioning of the packages. It was deemed necessary that the volume immediately adjacent to the burner be filled in order to encourage ignition. The charge was placed in the most favorable position to encourage ignition and burning. The incinerator charging door was closed and the test begun.

It was concluded that the ability to burn a difficult charge is indicated by the unit's ability to perform without attention. Therefore, it was determined that the load would not be agitated until burning had begun and ceased. If residual charge remained, it was weighed, the weight was recorded and the residue was returned to the incinerator chamber, again in a position favorable to ignition and combustion. No extra disturbance of the charge was permitted. This was repeated as often as necessary.

When the charge was completely incinerated, as indicated by CO_2 percentage returned to initial value, and/or when no further burning appeared possible, the test was considered to have been completed.

During the time of the test, periodic observations were made and recorded as follows:

(a) Check on gas rate
(b) Gas meter reading
(c) Static draft
(d) Smoke
(e) Odor
(f) Incinerator surface temperatures
(g) Progress and condition of burning
(h) General information

Floor, wall and stack temperatures were recorded continuously.

Definition

The gas-fired incinerators fall into 2 general classifications:

(1) "Dehydrating" (constant low Btu. input)
(2) "Rapid Combustion" (Limited time—high Btu. input)

The dehydrating type operates on the principle that by applying a constant low Btu. input the wet charge can be gradually dehydrated or dried and then ignited, from which point it will proceed to burn to completion. This type of incinerator utilizes a burner input of between 1500 and 3500 Btu./hr.

The rapid-combustion type operates on the principle that a high Btu. input (9,000 to 25,000 Btu./hr.) will allow dehydration and combustion to take place simultaneously, since the burning dry mass should help to dehydrate the remaining wet mass.

It is noted that in both types of incinerators it is necessary to dry the combustible before it can be burned. Very little combustion took place before the whole mass in the incinerator was dehydrated. This is quite reasonable since the heat of vaporization of water is very high and quite enough to prevent any appreciable rise in temperature of the surface of the garbage charge until after the moisture was evaporated. Of course, during this dehydrating period, vapors will be produced and will be vented to the stack. These vapors may be condensible greases and may well be odor sources in addition.

Test Loads

For purposes of evaluating stack, floor and wall temperatures, the following load was adopted from A. G. A. test procedure:

> "A charge of shredded newspaper equal to 2 lb., for incinerators with a capacity of 2 bu. or less, shall be introduced into the incinerator chamber intermittently at 6 min. intervals. For incinerators with capacities greater than 2 bu., the amount of news-

> paper shall be increased at the rate of 1 lb./additional bushel of capacity."

For purposes of evaluating the incinerating performance, the following materials and quantities were used:

For each bushel of rated capacity, seven $2\frac{1}{2}$ lb. packages of the following mixture, wrapped in 3 sheets of newspaper, were considered to be an adequate load for test purposes. The mixture, adopted from A.G.A. specifications, consisted of 20% by weight dried beet pulp, 5% laundry starch, 5% beef suet, and 70% water.

Discussion

Odors

It was noted throughout the testing that odors were emitted into the stack. Uusally the draft was sufficient to prevent odors from entering the test room. However, these odors were still present in the flue gases and were emitted from the stack. Although the test load used was not particularly offensive, a penetrating, relatively unpleasant odor was present in the flue gases.

The following quotation will serve to illustrate why it is almost certain that odors will be present:(1)

> "Combustion is not a method of odor control unless it is complete combustion. Even then, the burning of nitrogeneous and sulfurous organic matter with the evolution of pungent oxides of nitrogen and sulfur is not the ideal conclusion to an odor-destruction process, but slight nuisance is often preferred to the sickening offense of the unburned vapors. Partial combustion may be even worse than no combustion, as the neighbors of incinerators and rendering plants will testify. Incomplete combustion in Diesel and internal combustion engines yields irritating and sickening aldehydes with formaldehyde as the principal ingredient in the malodorous group."

To be realistic, the odor effect *may be reduced with complete* combustion. Even then odors will likely be present in sufficient concentration to be offensive.

It is argued by many that since the outside atmosphere is so vast, the nuisance degree of the domestic incinerator will be nil. However, this is apparently true only where the odors can be dissipated at high levels in a large fresh air area with reasonable wind velocity. Even then it is not true, since low stacks adjacent to other buildings can deliver the odors into the second story windows of the neighbor. In the case of a congested living area, where chimneys are close together and low, the author believes that it would be almost certain that the concentration of domestic incinerators planned would result in an air pollution problem of considerable magnitude.

Another quotation will be used to indicate that the odors noted during testing were inevitable with the present design of domestic incinerator:(2)

> "The minimum combustion temperature for the *complete* destruction of garbage, meat refuge, corn products, waste and the like, may range from 1400 F. to 2000 F. according to the type of waste so treated and the construction of the incinerator, cremator, or furnace. Even higher temperatures may be needed in some industries."

In view of the fact that the temperatures at the exit of the combustion chamber were quite low during the burning of the Wet Load, not over 700 F., and in most cases much lower, it is quite certain that odors would be present during most garbage burning.

It is possible that combustion could be completed if a secondary burner were used at the exit from the combustion chamber, but this was not done in any of the units tested. The odors noted during the test runs were definite and it can be seen from the above that unless the incinerator is designed for complete combustion and operated on refuse which does not produce such gases as sulfur dioxide, etc., as products of complete combustion, odors will be produced.

Even if the incinerator is designed and constructed for complete odorless combustion, the operator would be the housewife, who, in most cases, would not be skilled in the firing technique which would be required and she certainly would not invest the time and trouble necessary to follow firing methods required for complete combustion. In this the author does not intend to belittle the housewife, since he believes that the average husband could not do any better.

The author questioned a number of incinerator owners who were apparently good neighbors and ascertained that many of them did not use the incinerator for burning during periods of hot humid weather when the wind velocity was low.

It is also quite possible that a concentration of odors might result in a nuisance to surrounding communities.

Agitation of Test Load

It was observed during the tests using the simulated garbage that it was necessary to agitate the load since channeling occurred. Burning started in the vicinity of the burner and usually a hole was burned through the load to form a channel from the bottom to the top of the charge. The surfaces of the channel were crusted and coked, preventing the passage of gases through the charge. When this happened, combustion ceased for all practical purposes. In order to burn the charge completely, it was necessary to break up the caked surfaces and agitate the load.

Since this coking and channeling effectively prevented any further combustion, and was undesirable, an attempt was made to standardize the procedures by determining whether channeling occurred and if it did, then the load was shifted. No agitation was done unless combustion ceased as channeling occurred. This procedure was followed because it was felt by the author that automatic operation should involve no agitation. It is realized, of course, that the housewife will agitate the load to a certain extent when putting in refuse. However, it was observed during the test runs that unless careful firing procedures were followed, it was quite possible to have a considerable portion of the wet charge remain unburned until broken up or relocated in the incinerator. In most of the incinerators tested it was not possible to burn the mass completely without relocating it and usually there was a considerable mass remaining on the corners of the grate, remote from the burner, which for all practical purposes it was impossible to burn.

Condensible Greases

It was observed during the burning of the simulated garbage load that a considerable quantity of tars and greases condensed out on the cooler surfaces of the flue and stack. No attempt was made to measure these effects quantitatively. However, there was observed unmistakable evidence of condensible vapors in the flue gases. Since the stack used in this investigation was quite high, no evidence was obtained outside the building. However, it is believed by the author, from evidence obtained in these tests, that with lower stacks, as in smaller houses, the emission of condensible vapors will occur, causing undesirable deposits on the surrounding premises.

Conclusions

Based on the data obtained and observations made during the investigation and as a result of further study and analysis, the following conclusions are drawn:

Odors

It is the opinion of the author that it is not possible to operate any of the incinerators investigated in an odor-free manner.

There is little question concerning the ability of these units to keep the odors from being released into the room in which the incinerator is operated. However, this is not the only problem involved, since, if the odors are released into the chimney and are emitted into the outside air, then a concentration of units will result in an odor nuisance to the city itself and quite likely to surrounding communities.

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(1) McCord and Witheredge, "Odors—Physiology and Control," McGraw-Hill Book Company (1949) p. 170.

It is the author's opinion that with considerable research it may be possible to isolate and identify the more offensive odor producers in the flue gases. However, since the number of different products of combustion and distillation from the multitude of household wastes is practically infinite, the task is a difficult one which will involve considerable time and expense. Once the offenders are properly identified, it may be possible to design an incinerator with the means of eliminating the odor. Of course, the incinerator design will very likely become much more complicated and costly. The homeowner will still be the operator and in a position to operate the incinerator as an odor producer in spite of the best efforts of research and design.

TABLE I

General Information

Incinerator	Item	Observation
A	a	Hard to operate grate under load although grate principle is better than average.
	b	Door over controls unduly hard to close, and was damaged in closing.
	c	Controls entirely enclosed.
	d	Durable finish—undamaged in testing.
	e	Appearance—suitable for kitchen installation.
	f	Burned varnish on floor during burning of paper.
B	a	Controls entirely exposed.
	b	Appearance—suitable for basement only.
	c	Ash can fall around as well as into the ash pan.
	d	Burned varnish on floor during burning of paper.
C	a	Troubled by burner outage.
	b	Fire-brick damaged in operation.
	c	Appearance—suitable for kitchen installation.
	d	Finish—not durable.
	e	Controls completely shielded.
D	a	Troubled by burner outage.
	b	Controls entirely exposed.
	c	Paint burned around charging door and flue outlet.
	d	Appearance—suitable for kitchen installation.
E	a	Troubled by pilot outage.
	b	Charging door jammed due to expansion.
	c	Charging door falls shut and is a hazard.
	d	Appearance—suitable for kitchen installation.
	e	Local finish discoloration.
F	a	Top surface hot enough to ignite paper while burning dry load.
	b	Poor handles.
	c	Ash door flimsy.
	d	Body jacket flimsy.
	e	Troubled by pilot outage.
	f	Appearance—suitable for basement.
G	a	Lid temperatures reached 400 F. during burning of dry load.
	b	Controls completely enclosed.
	c	Paint burned off on ash door and around flue outlet.
	d	Plastic ash door handle melted off.
	e	Appearance—suitable for kitchen installation before finish damage.
H	a	Grate design faulty in that it did permit part of the unburned charge to be dumped into the ash pit prematurely.
	b	Outside surface of incinerator became too hot to touch.
	c	Controls completely exposed.
	d	Appearance—suitable for basement installation.
I	a	Handles too hot to touch during burning of wet load.
	b	Odors emitted to test room.
	c	Sharp edges and generally inferior workmanship.
	d	Ash pit door hard to open.
	e	Charging door has poor handle and is generally weak in construction.
	f	Controls completely exposed.
	g	Jacket paint softened during hot run.
	h	Appearance—suitable for basement installation.
J	a	Lid temperatures reached 525 F. during burning of dry load.
	b	Plastic handle on grate shaker softened, due to high temperature.
	c	Controls completely exposed.
	d	Appearance—suitable for basement installation.
K	a	Ash door—hard to open.
	b	Loading door casting poorly designed—broke at hinge.
	c	Ash can fall around as well as into the ash pan.
	d	Controls completely exposed.
	e	Appearance—suitable for basement installation.
L	a	Controls completely exposed.
	b	Entire incinerator became too hot to touch during burning of wet load.
	c	Appearance—suitable for basement installation.
M	a	Poorly designed charging door hinge.
	b	Sharp edges left on metal — workmanship inferior.
	c	Charging door handle discolored by high temperature—paper ignited on lid during burning dry load.
	d	Appearance—suitable for basement installation.
N	a	Loading door temperature reached 400 F.
	b	Plastic handle on loading door deformed, due to high temperature.
	c	Paint burned on ash door and around flue during testing.
	d	Controls completely exposed.
	e	Appearance—suitable for kitchen installation.

Smoke

The considerable smoke, including condensible vapors and greases emitted during the investigation of the incinerators, forces the author to conclude that the incinerators can be a source of smoke nuisance unless operated very carefully by a skilled operator. Since the housewife is not a skilled operator in the required sense, it is concluded that a smoke problem will result from wholesale installation in a concentrated area.

The following list indicates the significance of the smoke gage reference number:

Gage Number
1. Maximum permissible for pressure type oil burner
4. Maximum permissible for gravity type oil furnace
6. Maximum permissible for gravity type space heater

Temperatures in Stack

The high stack temperatures noted during the burning of the dry combustibles leads to the conclusion that a fire hazard may result from the proposed installation. Stack temperatures noted ranged from 970 F. to 1500 F. when burning the dry load. The stack temperatures must be high during combustion, since no heat transfer from the products of combustion occurs to cause the temperature of the gases to fall. Here the author wishes to call attention to the necessity for high combustion temperatures to complete burning, which, if accomplished, will likely result in a fire hazard. If the temperatures are low, then smoke and odors will result. Either condition is undesirable.

If the chimneys in all of the houses considered are equivalent to Class A chimneys and are in good condition, it is possible that no hazard will result. However, since it is believed by the author that a large percentage of the chimneys involved will not be equivalent to Class A, it is concluded that wholesale installation of incinerators will result in a real problem for the Fire Department unless extensive modifications are made to existing chimneys. Since it is not reasonable to rebuild chimneys which are possibly Class B or equivalent, or to convert them to Class A, the feasibility of wholesale installation is questionable.

Greases condensed out of vapors produced by incinerators will be deposited in the stack in appreciable quantity over a period of time. These greases were noted during testing and since they came from the suet in the test load, it was decided to determine likely ignition temperatures.

An open cup flash and fire apparatus

(continued on page 243)

Incidence of Mildew on Painted Surfaces*

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Elizabeth, N. J.

The Board of Health in any locality may be occasionally called upon to investigate discoloration of painted buildings. This discoloration may be caused by gaseous wastes from industrial plants or by mildew growth. In the first case, soot or sulfur containing fumes may cause paint discoloration. The latter, particularly, may be troublesome where buildings are painted with lead containing pigments. The solution to this problem is the use of lead-free or so-called "Fume-proof" paints if the level of pollution is not injurious to humans. There are instances, however, where the local industrial plant may be entirely blameless for paint discoloration. It is this aspect which is discussed in this paper.

Discoloration of paint due to mildew growth has long been recognized (Fig. 1). One of the first to make a detailed study of the problem was Dr. Haenseler at Rutgers University. It has been only in recent years that paint manufacturers have recognized the need to treat paint to prevent mildew. To many a home owner, the need to use mildew resistant paint may not be clear. A house is repainted about every 5 yr. and surely the kind of material in paint cannot offer much food to a fungus.

Conventional paint consists of vegetable oils and pigments. The pigments are generally inorganic and are not susceptible to mildew attack. The oils are derived from various plant sources and are susceptible to mildew attack in varying degrees. Formulation of the paint, that is, the type of oils and pigments used, is an important factor in the overall mildew picture. Paints which contain some zinc oxide and some heat-bodied oil are less likely to show mildew quickly than is a paint containing no pigment of this type and a good deal of raw linseed oil. There are also other factors which must be considered but these are beyond the scope of this paper.

In recent years, latex emulsion paints or water base paints have become increasingly popular for exteriors, particularly for masonry or asbestos cement shingles. These paints all contain thickening agents of plant or animal origin, thus making them susceptible to mildew.

In the past, the paint mildew problem was believed to be confined to the warmer humid areas of the country as Florida and the Gulf Coast. Studies by a number of laboratories have shown that mildew on paint occurs in all areas where relative humidity rises above 60%. In fact, some paint chips were received recently from Thule, Greenland. These were taken from buildings in that area and were found supporting mildew growth.

Paint supporting mildew growth has been encountered in all parts of the United States and Southern Canada. The only exception is the arid Southwest United States.

Depending upon the type of paint used, infection with mildew may occur within a matter of a few months or it may not occur for several years. The types of fungi growing on paint are varied. On exterior paints, one type of fungus known as *Pullularia pullulans,* is found in about 95% of the cases. This has been confirmed by over 5 yr. of study and examination of several thousand paint chips and exterior paint panels exposed in various parts of the United States. This fungus gives the painted surfaces a gray or black appearance. In addition to simply discoloring the paint, this fungus may also disrupt the paint film so that the protective qualties of the coating are impaired.

Another type of fungus sometimes found growing on exterior paints is one having the descriptive name, *Phoma pigmentivora.* This forms an oil soluble reddish-purple pigment which diffuses through the paint. This type of infection has been found mainly in the Great Lakes region although we have seen it occasionally in this area. It is a strikingly different type of mildew attack. When it occurs, no other type of fungus is usually found associated with it. Very often the entire house will be purple colored. The eradication of this organism is no more difficult than is any other. However, because of the oil soluble nature of the pigment, it may bleed through a new coat of paint even though the organism is no longer alive. Special sealing coats of paint must be used in this case.

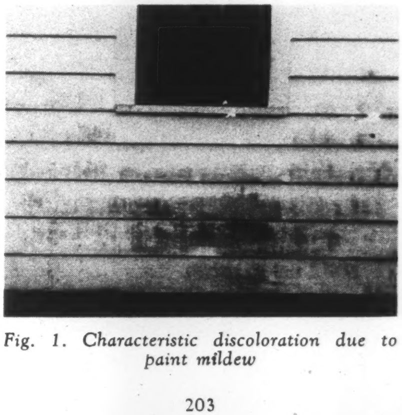

Fig. 1. Characteristic discoloration due to paint mildew

Until recently, it was not easy to distinguish mildew from dirt. Recourse to microscopic examination was necessary. For positive identification, it is still necessary. For on-the-spot detection of mildew, a simple test has been developed(1). It is not a quantitative measure of the degree of mildew versus dirt but is intended to show when the major cause of discoloration is fungal in nature. The reagents used are simple—a solution of 5% sodium hypochlorite (bleaching fluid) and water. A drop of the hypochlorite is placed upon the suspected surface. If it bleaches to the color of the paint, the discoloration is most likely mildew. If it is dirt, it will not bleach out. (Figs. 2 and 3). The water is used to remove the hypochlorite. Some 600 different paint samples suspected of being mildewed have been tested. Where the cause was mildew, the characteristic bleaching was obtained. In 96% of such cases, the presence of mildew was confirmed by microscopic examination. It is a handy technique for the man in the field.

In the laboratory, microscopic examination is preferred for positive identification. With this instrument, dirt can be readily distinguished from mildew and the relative ratio of each determined. The filamentous growth and the characteristic reproductive structures of fungi are easy to recognize after a little experience (Fig. 4). In some instances the filamentous structure is lacking and only spores may be seen. This happens with Pullularia and requires some skill

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*Presented at the 1st Air Sanitation Seminar of the Mid-Atlantic States Section of APCA, Rutgers University, April 13, 1955.

(1) Klens, P. F., Leitner, G., and Snyder, H. D., "A Field Method for Detecting Mildew on Paint," *Amer. Paint J.*, **38**, 76 (June 14, 1954).

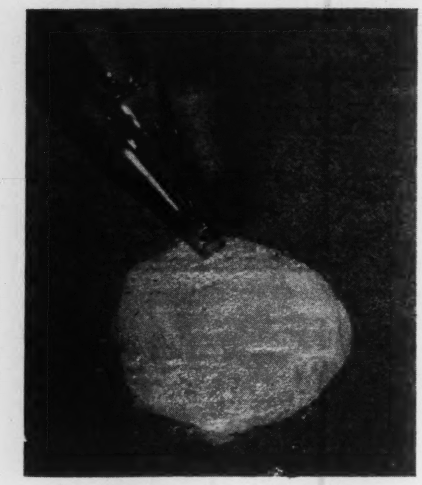

Fig. 2. Bleach test showing positive reaction indicating mildew growth

to distinguish this type of growth from dirt. In our laboratory, a monocular microscope equipped with a metallographic type lens is used. This allows light to be directed down through the lens onto the surface being examined. This permits examination of opaque objects such as painted surfaces. The following photomicrographs made with this equipment depict discoloration due to dirt and discoloration caused by mildew (Fig. 5).

We have discussed the cause of mildew and how it can be identified. Control of mildew on exterior paint surfaces must begin when the paint is applied. Washing or disinfecting a mildewed surface will only serve as a temporary corrective measure. Within a few weeks after such treatment, the mildew will recur. Since paint contains nutritive materials for fungi, it is necessary to incorporate toxic materials into the liquid paint. These compounds must remain active after the dried film is formed. Since the largest volume of exterior paint is white, ideally a paint fungicide should not discolor the paint. In addition, it should not affect the normal paint properties such as viscosity, drying, gloss and weathering characteristics.

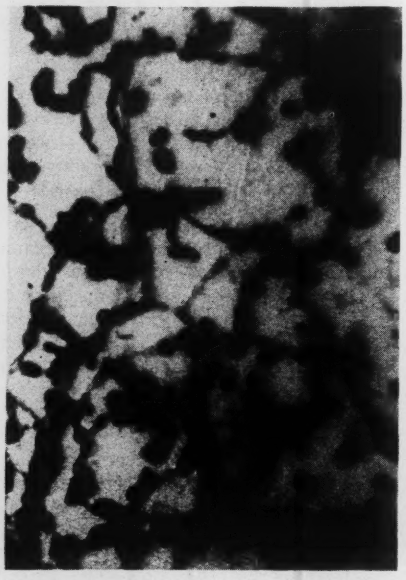

Fig. 4. Growth of Pullularia pullulans on a paint film

The compounds most widely used as paint fungicides are the phenyl mercurics. Many of these have little effect upon paint properties. In addition, at the concentrations used, 0.5% to 2.0%, they present no health hazard. The phenyl mercury compound with which this laboratory is most familiar has been tested for toxic effects and has been found to be safe to humans under conditions of use. In fact, a man weighing 60 k. would have to eat the solids in 1 qt. of paint containing 2% of the fungicide before toxic effects would occur. Further, at the level normally recommended, 0.5%, no dermatitis has been reported.

In addition to the phenyl mercury compounds, certain copper compounds are used. These, however, discolor the paint and cannot be used where a true white is required. They are also somewhat more expensive than the mercury compounds mentioned and therefore cannot compete for the broad market.

As mentioned previously, incorporation of a fugicide into the paint is not the complete answer to mildew although it is the most important factor. The paint chemist must use ingredients in the paint which will minimize the tendency to mildew attack. Over 400 paint companies in this country are offering mildew-resistant paint to home owners. These companies range from the large nationally-known brand names to the small local paint manufacturer around the corner. Some identify their house paint as "mildew resistant" while others incorporate it into their best quality house paint without mentioning it in their advertising. Mildew resistant paint is available in practically every city and town in the country. The use of such paint will give the home owner a more durable and economical finish. It will also eliminate many problems for the air pollution investigator.

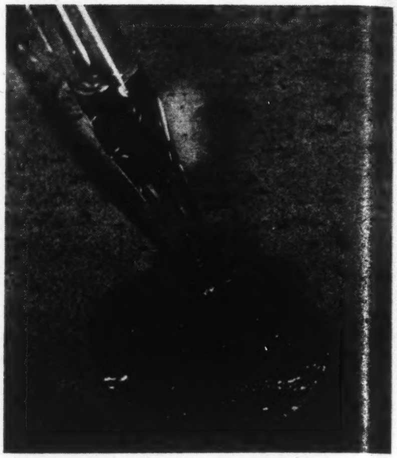

Fig. 3. Bleach test showing negative reaction indicating discoloration due to dirt rather than mildew

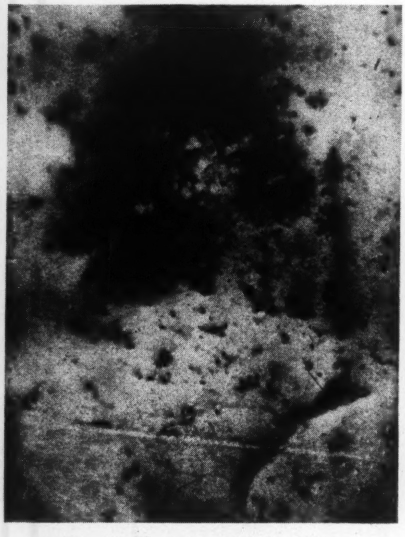

Fig. 5a. Photomicrograph of dirt

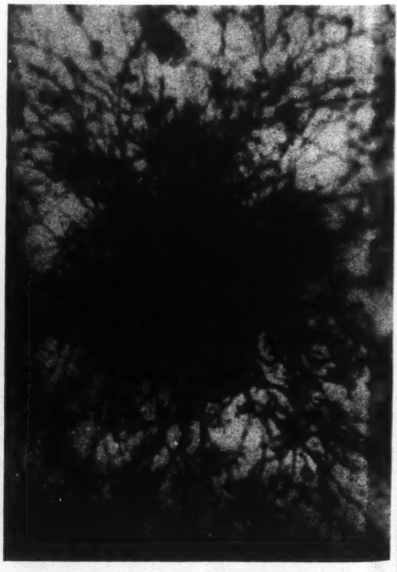

Fig. 5b. Photomicrograph of mildew

The Invisible Injury Theory of Plant Damage*

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The "invisible injury" theory of plant damage, mentioned originally by Ramann and Soraurer, was developed by J. Stoklasa⁽¹⁾, who believed that toxic gases in the atmosphere (particularly sulfur dioxide) could cause severe damage to vegetation even though the concentration was below that needed to produce visible lesions on the leaves of the plants. The following quotation from Stoklasa's book, published in 1923, summarizes his concept:

> "The invisible injury which, in general, is present wherever sulfur dioxide travels and even where no acute or chronic injury is currently evident, deserves the greatest attention, because the vegetation under such conditions will be damaged and the photosynthetic processes disturbed by the sulfur dioxide. The premature autumn coloring of the leaves can be ascribed in many cases only to the harmful action of the sulfur dioxide. That the whole growth and functioning of the plants in industrial cities in the vicinity of factories cannot proceed normally, I have been forced to accept from my water culture experiments and the behavior of the experimental plants. Great differences in the over-all development of the plants, in the activity of their photosynthetic apparatus, and particularly in the total growth, cannot be missed by a keen observer who knows plant life. That enormous losses arise from invisible injury, is clearly evident.
>
> "It remains to note especially, that owing to invisible injury of the plant structures, resistance against infection by plant parasites is lost. The needles of certain conifers, growing in the neighborhood of factories whose gases cause plant damage, were not injured, but pines were observed to have succumbed to the fungus disease, 'Rostpilz' (Chrysomyxa Ledi). The parasite invaded through stomata into the parenchyma and palisades cells, and the chlorophyll was completely destroyed. We can also determine a great enrichment of sulfate in the needles of these conifers, which indicates that sulfur dioxide and sulfuric acid will be absorbed by the plant tissues, even though they are present in the air only in extreme minimal quantities . . .
>
> "A communication from Forester Gerlach in Waldenburg concerning the appearance *en masse* of insects as a characteristic sign of smoke damage in pine and spruce forests, is of the greatest significance . . ."

From these quotations and other statements in the text, it appears that Stoklasa associated invisible injury with (a) a reduction in the photosynthetic activity of the plants, (b) a build-up of sulfates in the leaves, (c) early senescence, (d) an over-all unthrifty appearance of the vegetation without actual lesions on the leaves, (e) reduced growth and reduced yield, and (f) increased susceptibility to disease and invasion of parasites and insects.

Stoklasa showed that respiration of spruce was inhibited by sulfur dioxide. He concluded that photosynthesis would also be inhibited. His experimental work was done with unrealistically high concentrations of gas and will not be discussed here. His observations, showing a build-up of sulfur in the leaves of plants growing in the field, and also premature senescence due to long-continued low concentrations of the gas, are in accord with general experience. Premature senescence is not, strictly speaking, invisible injury unless it can be shown that the activity of the leaves is reduced before they begin to show symptoms of senescence. It seems probable that the unthrifty condition and reduced yield of vegetation in industrial smoke areas are due to other constituents of the smoke besides sulfur dioxide when the concentrations of the latter are small and characteristic sulfur dioxide lesions are absent. The reduced resistance to disease and invasion of insects and parasites has not been experimentally connected with sulfur dioxide in any known case, and in a few cases evidence to the contrary is strong. The converse is often true: diseased plants may be more sensitive to gas damage than healthy plants.

Of the air pollutants in addition to sulfur dioxide which are suspected of causing "invisible injury," hydrogen fluoride, coal smoke, and "smog" have been studied to a limited extent. The gases like ethylene, which cause epinasty and nutation, need to be considered also. This paper will summarize the present state of our knowledge of these pollutants in relation to "invisible injury." The latter is defined as interference with growth, photosynthesis, respiration, reproduction, or enzymatic function or demonstrable increase in susceptibility to disease, without attendant lesions or discolorations on the leaves, stems, or roots of the plant.

Sulfur Dioxide

The "invisible injury" theory as applied to sulfur dioxide has been of great concern to industry, particularly the smelting industry, in the United States and Canada for the past 40 yr. This industry, faced with claims for crop damage and with litigation, was puzzled to know how to define its responsibility if the area of plant injury was actually greater than the area with visible lesions.

A number of investigations during this period have satisfactorily clarified the case of sulfur dioxide. In 1915, the Selby Smelter Commission carried out an extensive fumigation program on field plots of barley which showed that treatments which did not cause visible lesions on the leaves, did not reduce either the growth of the plants or the yield of grain. Similar results with grain and many other crops were obtained by American Smelting and Refining Company, the National Research Council of Canada, and Boyce Thompson Institute.

The problem was attacked more intensively starting in 1933⁽²⁾ by American Smelting and Refining Company with new carbon dioxide analyzers, by means of which respiration and photosynthesis of plants growing under field conditions could be measured continuously and automatically. This was done by passing a measured volume of air through a fumigation chamber and measuring the carbon dioxide content of ingoing and outgoing air. From these data the rates of assimilation and respiration could be calculated. Sulfur dioxide could then be added to one plot for comparison with another similar plot without sulfur dioxide. The Canadian National Research Council⁽³⁾ did similar experiments in 1936-37 and came to similar conclusions.

In the A.S. & R. experiments, alfalfa was treated continuously day and night with 0.08-0.22 ppm. sulfur dioxide for over 6 wk. without reducing the photosynthetic activity of the plot, though the older leaves became senescent somewhat earlier than on the check plot. Fig. 1 shows the hr.-by-hr. values of the carbon dioxide exchange of fumigated and check plots from the 28th to the 37th day of continuous fumigation, and Fig. 2 gives the daily sums of respiration and

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⁽¹⁾ Stoklasa, J., "Die Beschadigung der Vegetation durch Rauchgase und Fabriksexhalationen," Urban und Schwartzenberg, Berlin (1923).

* Presented at the 48th Annual Meeting of the Air Pollution Control Association at Detroit, Michigan, May 22-26, 1955.

⁽²⁾ Thomas, M. E. and Hill, G. R., "Relation of Sulfur Dioxide in the Atmosphere to Photosynthesis and Respiration of Alfalfa," *Plant Physiol.* 12, 309-83 (1937).

⁽³⁾ Katz, M., Ledingham, G. A., and Harris, A. E., "Carbon Dioxide Assimilation and Respiration of Alfalfa under Influence of Sulfur Dioxide," Effect of Sulfur Dioxide on Vegetation, Nat. Research Council, Canada Pub. No. 815, 393-428 (1939).

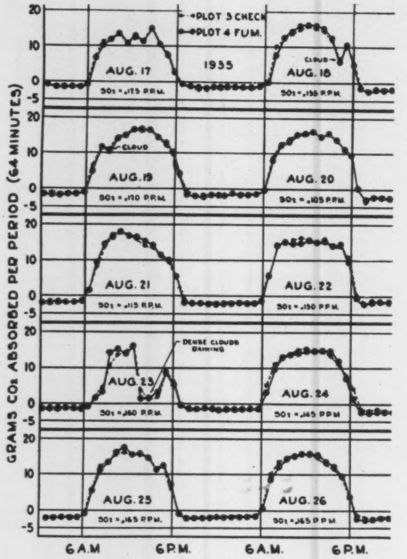

Fig. 1. Respiration and photosynthesis of 2 plots of alfalfa measured simultaneously. Plot 4 was fumigated with the indicated concentration of sulfur dioxide. Plot 3 was the control. Graph presents the detailed data from the 28th to the 37th day of a 45-day continuous fumigation.

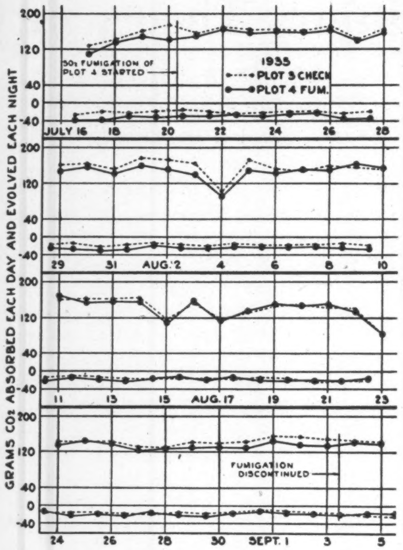

Fig. 2. Daily respiration and photosynthesis values of the check and fumigated plots during the 45-day fumigation experiment illustration in Fig. 1.

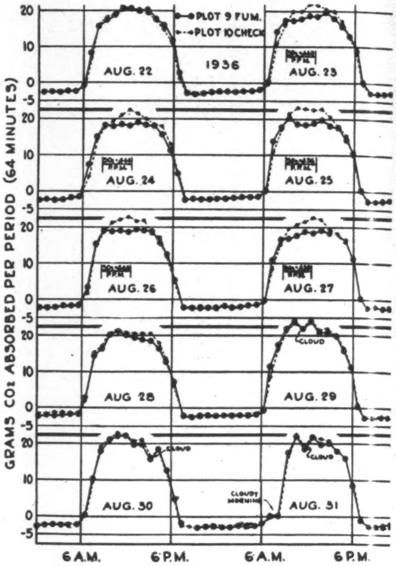

Fig. 3. Respiration and photosynthesis of a pair of plots, 1 of which was fumigated with .45 ppm. SO_2 for 4 hr./day on 5 days. Five additional similar fumigations had been applied earlier to this plot.

photosynthesis during the whole experiment. There were some slight shifts in the relative activities of the 2 plots, but it is evident that this protracted fumigation treatment had no significant effect on the rate of photosynthesis of the treated plot.

Higher concentrations could be tolerated for shorter periods, but after a few minutes to several days, depending on the concentration, photosynthetic activity fell off while the gas was present and rose again when the fumigation was stopped. At about 0.2 ppm. continuous fumigation had no effect for about 10 days; during the next 2 wk. at this concentration, however, photosynthetic activity fell off gradually by about 10%. A continuous fumigation at 0.3 ppm. reduced the photosynthetic level by 25% in the course of 2 wk. This was partly due to leaf damage, but also partly to sulfite in the leaves which was not oxidized as rapidly as it was absorbed, as may be seen by the fact that the level of activity rose 7% when the fumigation was discontinued. Concentrations of 0.3-0.4 ppm. for about 4 hr./day were tolerated for over a month without significant reduction of photosynthesis. At about 0.45 ppm. for 4 hr./day (Fig. 3), photosynthesis was definitely reduced during the time the gas was present. However, if the fumigation was discontinued before lesions were produced, the photosynthetic activity returned rapidly to its normal level, or even at times to a level slightly higher than normal, usually within one or two hours. The net loss of assimilation was hardly measurable, even after ten such fumigations.

At 0.6 ppm. sulfur dioxide for 4 hr./day, inhibition of photosynthesis, was appreciably larger than at 0.45 ppm. (Fig. 4). The level of assimilation was reduced 25% while the gas was present. Six such fumigations during a period of 2 wk. reduced total assimilation by 10%, equivalent to about 5% for the crop. There was 2.5% of leaf destruction. The yield of the fumigated plot was 14% less than the check, due partly to the fumigation and partly to a less dense growth of alfalfa plants.

At still higher concentrations, the effects were greater, but essentially similar (Fig. 5). A 12 min. fumigation with 8.5 ppm., which caused 3% destruction of leaf area, reduced the photosynthetic level to ⅓ its prefumigation value, and complete recovery required 2½days. Another fumigation with 1.9 ppm. for 70 min., which caused 14% leaf destruction, reduced assimilation to 12%, and recovery required more than 1 day. It is of interest to note that the calculated reduction of yield of this crop based on the leaf destruction agreed well with the actual yield.

A small amount of temporary reduction of photosynthesis which Stoklasa might interpret as "invisible injury" is suggested by these experiments when the sulfur dioxide fumigation exceeds a threshold concentration. Under these conditions it appears that sulfurous acid or sulfite can accumulate in the cells of the plants and inhibit photosynthesis without necessarily killing the cells. At sub-threshold concentrations, the sulfite is oxidized to the non-toxic sulfate as rapidly as it is absorbed, so that inhibition of photosynthesis does not occur. At high concentration, the killing action of the gas is so rapid that exposures must be of short duration in order to obtain temporary inhibition of photosynthesis rather than death of the cells. In this case there is often a temporary plasmolysis of the cells with subsequent recovery of turgidity if the amount of sulfur dioxide absorbed is not too great. Evidently, complete restoration of the photosynthetic function to these cells after temporary plasmolysis requires considerable time, up to 2 or 3 days.

The conclusion seems to be definite that "invisible injury" due to sulfur dioxide is a second-order effect at most, so far as the physiological activity of the plant is concerned. No observations have been recorded in recent decades to suggest that the gas makes the plants more susceptible to disease or attacks by fungi or insects, and there are some observations to the contrary, for example, on Verticellium wilt of cotton. However, very little direct research has been done in this field, so a definite conclusion regarding this phase of Stoklasa's postulate is not possible at this time.

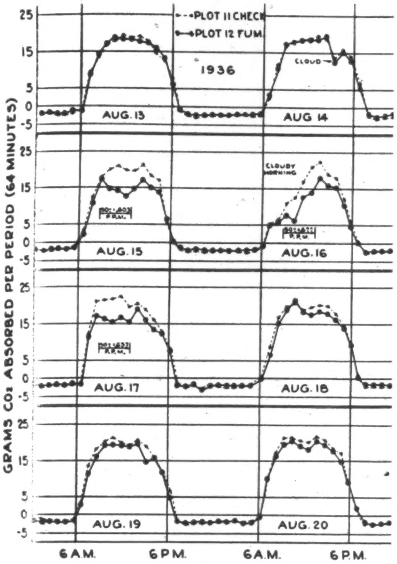

Fig. 4. Respiration and photosynthesis of a pair of plots, 1 of which was fumigated about 4 hr./day on 3 days at about .6 ppm. Three additional similar fumigations had been applied earlier to this plot.

Hydrogen Fluoride

The "invisible injury" theory as applied to hydrogen fluoride has been studied to a limited extent only. This gas differs considerably from absorbed sulfur dioxide in that the latter is readily oxidized to the much less toxic sulfate, whereas fluoride cannot be disposed of so easily after absorption into the leaf. Fluoride tends to translocate to the margins and tips of the leaves, where lethal concentrations are readily built up, causing acute injury to those tissues but leaving non-toxic concentrations in the remainder of the leaves. In extreme cases, the fluoride concentration in the tips and the margins may be 3 to 100 times as great as in the body of the leaf. Similarly, different species of plants vary enormously in their susceptibility to fluoride, some requiring 100 times the fluoride concentration to cause injury that others require. A few measurements of photosynthesis have been carried out on gladiolus and a number of other plants fumigated with hydrogen fluoride. Unfortunately the detailed data of these experiments are not available for publication. The following quotation from the forthcoming Air Pollution Handbook (to be published by McGraw-Hill Book Company)⁽⁴⁾ summarizes these experiments.

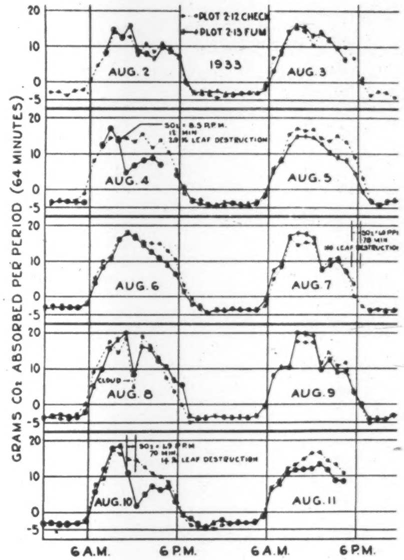

Fig. 5. Respiration and photosynthesis of a pair of plots, 1 of which was fumigated 3 times with 1.0, 1.9 and 8.5 ppm. SO_2 on 3 days.

"The toxicity of low concentrations of hydrogen fluoride to a few species and the apparent lack of toxicity to most other species, raise the question, whether 'invisible injury' is produced by this gas, as was claimed by Stoklasa for sulfur dioxide. Exploration of this field is in its initial stages, but photosynthesis data so far obtained with gladiolus, fruit trees, barley, alfalfa, and cotton indicate that 'invisible injury' does not occur until the concentration of the gas exceeds a threshold value for each plant. With higher concentrations there may be a temporary reduction of photosynthesis, without corresponding acute injury as was observed with sulfur dioxide fumigations. However, recovery from the fluoride treatment is much slower than from the sulfur dioxide; therefore the fluoride treatment may cause a small but significant reduction in assimilation. This difference in rate of recovery is probably explained by the fact that whereas sulfite in the leaves is rapidly oxidized to the relatively non-toxic sulfate, a photosynthesis-inhibiting concentration of fluoride in the tissues can only be removed by the slower processes of translocation, volatilization, and possibly reaction with organic compounds in the leaf.

"Many plots of different varieties of gladiolus have been fumigated for a number of days with about 1-10 ppb. of hydrogen fluoride. So long as no visible injury was produced there was no decrease in the rate of carbon dioxide assimilation. In one experiment, a plot of the sensitive variety, Surfside, was fumigated 6 to 7 hr. each day, 5 days a wk. for over 2 mo. After the first 7 days, injury began to appear at the tips of the blades and gradually extended down the blades until 45% of the leaf area was destroyed. Careful measurements of the area injured were made at intervals. The rate of photosynthesis and percentage of intact tissue followed each other faithfully throughout this period. For example, 45% leaf destruction reduced photosynthesis about 45%. It is to be noted that most of the absorbed fluorine was found in the injured areas. The functioning areas had much lower concentrations. Higher concentrations of hydrogen fluoride (12-30 ppb.) caused a sharp reduction in photosynthesis followed by a rapid recovery at first, then a gradual increase, until the level was reached corresponding to that expected from the amount of leaf destruction caused by the fumigation. Similar responses were shown by fruit trees at 20-50 ppb., by young barley at 68 ppb., and by alfalfa at 250-1100 ppb. in 4-8 hr. fumigations. These effects were equivalent to a total interruption of photosynthesis for a few hours to 2-3 days. The photosynthesis of cotton was not significantly affected by concentrations of hydrogen fluoride up to 500 ppb. Higher concentrations (500-1100 ppb.) interfered temporarily to some extent, but when the fumigation was stopped before causing injury, the photosynthesis returned to its original level in a few hours."

The over-all effect of a series of fumigations, each of which reduced photosynthesis to an extent greater than the amount of leaf destruction produced, cannot be evaluated at this time. Even the effect of a single fumigation is uncertain. Reduction of photosynthesis equivalent to 3 days of darkness might be expected to reduce assimilation about 3% for a 100-day plant and 10% for a 30-day plant. One might also expect a corresponding reduction in yield of a vegetative crop. The effect on a fruiting crop is unpredictable: it might range from no reduction at all in yield to a definite loss, depending on whether excessive abscission of the fruit occurred. Of course, if such abscission did occur—and no information is available to indicate that this might happen in the absence of severe leaf lesions—the injury would not be invisible.

Much work remains to be done in this field. Photosynthesis data for many crops are needed to determine threshold concentrations. It would also be necessary to know the atmospheric hydrogen fluoride concentrations in the field in order to determine which crops might have been subjected to "invisible injury" because their threshold concentrations were exceeded. With these data, it should be possible to estimate the extent of crop damage due to hydrogen fluoride with considerable assurance.

Smoke and Smog

It has been generally assumed that coal smoke has little effect on the growth of plants beyond the reduction which would be expected from reduced light intensity or interference with photosynthesis caused by deposition of solids upon the leaf surface. Bleasdale⁽⁵⁾ has shown (Table I), however, that when rye grass grown in greenhouses supplied with washed and filtered air is compared with plants grown in greenhouses

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⁽⁴⁾ Thomas, M. D., and Hendricks, R. H., "Effect of Air Pollution on Plants," Chpt. 9, Air Pollution Handbook (Magill, P. L., Holden, F. R., and Ackley, C., Eds.), McGraw-Hill Book Co., New York. In press.

⁽⁵⁾ Bleasdale, J. K. A., "Atmospheric Pollution and Plant Growth," *Nature* **169**, 376-77 (1952).

TABLE I

Effect of Scrubbing Polluted Air With Water on the Growth of Rye Grass in Manchester, England (After Bleasdale, 1952)

Date of Beginning	Duration (Days)	Soil Fertility	Dry Weight per Plant		Difference (%)	Difference for Significance at P=.05 (%)
			Scrubbed Air (mg)	Polluted Air (mg)		
Aug. 10, 1950	46	High	341±15[a]	280±13[a]	18	12
Oct. 6, 1950	75	High	99±10	72±7	27	28
	75	Low	73±4	59±2	19	12
Dec. 20, 1950	81	High	57±2	33±3	42	24
	81	Low	35±3	22±1	37	20
Mar. 16, 1951	77	High	817±74	825±1	—1	20
	77	Low	542±45	345±34	36	23
June 5, 1951	63	High	1084±55	673±112	38	26
	63	Low	728±35	287±46	61	18
Avg.	68	High			31	
	74	Low			38	

[a] Standard Deviation

supplied with the smoky air of Manchester, England, a very definite deficiency of growth could be ascribed to the smoky air without the appearance of any lesions on the leaves. This experiment seems to suggest that "invisible injury" is involved in the action of urban smoke, principally coal smoke, upon plants. The sulfur dioxide level in this smoke was too low to be of significance in reducing the photosynthetic activity of the plants. It is not uncommon to note an unthrifty condition in trees that have received an appreciable amount of smoke from nearby domestic chimneys or from the burning of trash. Again, sulfur dioxide is probably not a significant factor in causing the unthrifty condition.

In Los Angeles it has been observed that passing air through carbon filters greatly improves the growth of plants as compared with growth in unfiltered smoggy air. Differences in growth rate of tomatoes of as much as 25% of the dry weight have been reported by Koritz and Went(6) as a result of fumigations with "artificial smog" for 1 hr./day on 6 successive days (Table II). Hull and Went(7) did additional experiments in Pasadena using outside air filtered through charcoal and other media, notably steel wool mixed with iron filings and mossy zinc. After 5½ to 8 wk. exposure, carbon-filtered air gave much larger plants than any of the other media except the steel-iron-zinc mixture, which was nearly as effective as the carbon filter. Improvement in growth was most marked with endive and alfalfa. These were several-fold larger than the controls. Growth of sugar beet and tomato was also unmistakably improved.

Measurements of photosynthetic activity have not been made directly with smog, but if the growth rate is reduced this would necessarily mean reduced photosynthesis or increased respiration or both. Accordingly, it would appear that with both coal smoke and smog, such as exists in Los Angeles, there may be significant "invisible injury" to the vegetation. In addition, the Los Angeles smog causes characteristic lesions which would reduce photosynthesis still more.

The mechanism of the injury due to smoke and smog has not been worked out. Organic compounds such as the peroxides of peroxy acids with or without ozone are thought to be the principal phytotoxic materials in smog. They result from photochemical reactions between innocuous organics like hydrocarbons and oxides of nitrogen. Coal smoke might contain some of these photochemical reactants. More likely, its properties are due to appreciable amounts of moderately toxic compounds like formic acid, ethylene, aldehydes, ketones, chlorinated compounds, heterocyclic bases, etc. Ethylene is particularly interesting because it induces reversible nutation and epinasty(8), sometimes at very high dilution (0.05 to 0.1 ppm.). Mild exposure to this gas might cause "invisible injury."

Summary

In summary, it is evident that "invisible injury," as described by Stoklasa, may attend, to a very limited extent only, the reducing conditions which characterize sulfur dioxide fumigations. The oxidizing conditions in smog seem to be more effective in causing invisible injury, possibly because the normal reductive processes in the leaf are less intensive than the oxidative processes. Toxic fluoride ions have to be disposed of by rather slow mechanical means like translocation and volatilization, and therefore permit some "invisible injury" when threshold concentrations are exceeded. Toxic organic compounds in smoke are more difficult to characterize because their identity has not been definitely established. Presumably they represent a wide spectrum of compounds which would have to be inactivated primarily by chemical means. They might therefore interfere appreciably with the normal reactions in the leaf and cause some "invisible injury."

Finally, the reversible character of "invisible injury" when the toxic agent is removed, needs to be emphasized. This has been shown clearly with sulfur dioxide and hydrogen fluoride. Some of the experiments of Hull and Went suggest a similar reversal for smog. There is no definite information on this subject for the toxic constituents of smoke, but it seems unlikely that a permanent lowering of the activity of the leaf could occur without visible lesions.

TABLE II

Effect of Smog on the Growth of Tomato Plants (After Koritz and Went, 1953)

Treatment	Height (cm)	Dry Weight—50 plants	
		Tops (g)	Roots (g)
Control	14.92±0.32	1.24±0.02	0.52±0.04
Smog	12.54±0.31	0.94±0.07	0.42±0.05

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(6) Koritz, H. G., and Went, F. W., "The Physiological Action of Smog on Plants. I. Initial Growth and Transpiration Studies," *Plant Physiol.* 28, 50-62 (1953).

(7) Hull, H. M., and Went, F. W., "Life Processes of Plants As Affected by Air Pollution," Proc. Sec. Nat. Air Poll. Sym. pp. 122-28, Stanford Research Inst., Los Angeles, Calif. (1952).

(8) Crocker, W., Hitchcock, A. E., and Zimmerman, P. W., "Similarities in the Effects of Ethylene and the Plant Auxins," *Contrib. Boyce Thompson Inst.* 7, 231-48 (1935).

The Control of Atmospheric Pollution*

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The study of the air pollution problems of London, Los Angeles, Pittsburgh and a few other cities in the United States has fairly well defined the physical and chemical properties of the atmospheric pollution in the respective areas. Steady progress has been made in instrumentation and identification procedures which enable the control official to make a community survey or to evaluate the pollution problem from a single source.

Control Measures

Once the nature of the problem is determined and the sources and weather facts are evaluated, control measures can then be devised to relieve the detrimental effects resulting from atmospheric pollution. Where prolonged inversion conditions create a community problem, the effects can be minimized only by a control program against all air contaminants. Single sources may be treated to relieve local nuisance conditions. Regardless of the degree of control measures required, 3 basic methods can be applied to reduce the various contaminants which may be conveniently classified as aerosols, vapors and specific gaseous contaminants⁽¹⁾.

1. Reduction at the source is accomplished by the installation of collection equipment, improving the design of basic equipment, or through operational changes which inhibit the discharge to the atmosphere.
2. Dilution of the source is accomplished by using sufficient air to make the discharge unobjectionable. Tall stacks illustrate one means of applying this principle.
3. Allocating the use of the land to prevent harmful concentrations from occuring at a single source or from an area having many sources can be an effective measure. In applying this principle, the mass rate of emission from an area is prorated over the acreage utilized by the sources. Either the acreage to be occupied or the total contaminants discharged can be regulated to avoid harmful concentrations. The mass discharge will be governed by the total activity in a given area.

Equipment designed for the control of aerosols is based upon some physical mechanism of entrainment separation. The principal types of collection equipment are described in Table I. The size and density of the material which is to be collected is an important factor in determining the type of collector. In Table I the data must be considered as representative and not all-inclusive. Efficiency figures include ranges in which operation may be considered feasible. Cost figures, as well, show the general range and include appurtenances⁽²⁾.

Centrifugal Collectors

1. The centrifugal collectors are those used to separate that category of particulate material normally classified as dust from the exhaust stream. They are low in initial cost, simple in construction and provide for dry and continuous discharge of the collected material. Collection efficiencies are definitely low for material of small particle size. They may be used to advantage in a 2-stage collection system where dust concentrations are high.

Electrical Precipitators

Precipitators are of 2 distinct types. The single-stage or heavy-duty type is a high voltage device in which the charging and deposition of particles take place simultaneously. Voltage ranges from 30,000 to 100,000 v. This type is used in conjunction with electric steel and open hearth furnaces, gray iron cupolas, blast furnaces, non-ferrous primary smelting, cement manufacturing, catalyst dust recovery, sulfuric acids and fly ash from coal burning operations. This equipment has the advantage of large volume capacities in performance with high collection efficiencies over a wide particle size range. Operations may be sensitive, however, to such factors as conductivity of deposited dust, gas temperature, humidity and other items. The 2-stage precipitator charges the particles in one section and collects them in a succeeding one. Voltages are lower with closer electrode spacing and seldom exceed 13,000 v. They are normally limited to light-duty air cleaning but may be used for mists.

Cloth Filters

These collectors are used for the high efficiency removal of solid aerosols when an appreciable fraction of the emissions have a particle size smaller than 10 μ. The temperature of the exhaust stream must be maintained below 500° F. even for the most resistant filter mediums, and excessive humidity or entrained moisture must be avoided. High dust concentrations require increased filter area. Under these conditions, cloth filters are often used as a secondary unit in 2-stage collection systems where they follow a centrifugal collector.

Wet Collectors

Wet collectors are used in the control of dusts, mists and fogs. The liquid medium normally serves as the means of increasing the particle size of the contaminant aerosol to be removed, thereby facilitating separation from the exhaust stream. The liquid may be used to remove continuously collected material from impaction surfaces and to prevent reentrainment. Efficiencies are not high for dust except in devices with high energy input. Wet collectors may be used advantageously for soluble contaminants or in the cases of high dust loadings where large particle size is predominant.

Vapor Control

The control of specific gaseous air contaminants and vapors depends upon a wide range of conditions. Quantities of material vary from a few pounds of highly odoriferous material to tons of gaseous products which require collection. Furthermore, the concentration of contaminants at the source to be controlled may range from a few ppm. to 100%. The sources, as well, vary widely as to type and include such things as commonly observed plumes from stacks, storage tanks, stock piles, open sumps and many others. This great variety of operations and conditions clearly indicates the need for engineering evaluations of design for each separate installation considered. Such classifications can be accorded to this subject as shown in Table II. No attempt is made to show the efficiency or cost of control of gases

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⁽¹⁾ Larson, G. P., "Smokes and Fumes," Encyclopedia of Chemical Technology, The Interscience Encyclopedia, Inc., Vol. 12, pp. 558-73, 1954.

* Excerpts from a paper presented before the National Convention of the American Association for the Advancement of Science, Section M, Symposium, at Berkeley, Calif., on Dec. 30, 1954.

† Formerly Director of the Los Angeles County Air Pollution Control District.

⁽²⁾ Chemical Engineer's Handbook (Perry, J. H. ed.) 3rd ed., pp. 1013-50, McGraw-Hill, New York, 1950.

and vapors because the applications vary so widely.

Design of Basic Equipment

Careful consideration of the design of basic equipment can result in marked reductions of atmospheric pollution. As an illustration, combustion equipment in most processes can be so designed and operated as to minimize the discharge of air contaminants. When the economics of heat recovery is either secondary or of no consideration, modification in the furnace design can be effective in reducing the discharge of aerosols or smoke. The products of incomplete combustion of solids as well as odoriferous acids and aldehydes can be eliminated in most processes by giving careful consideration to the proper design principles. Time, temperature and turbulence are the 3 main factors to balance for a given air to fuel ratio in furnace design and thus effect complete combustion(3). Overfire steam jets, air distribution control and secondary combustion chambers represent appropriate design features to consider. The best engineering considerations, however, in these classes of combustion equipment cannot overcome the many deficiencies of operators in maintaining and properly operating the equipment. Education and training programs for operators are essential parts of any control effort by industry or government.

Dilution of the Source

Theoretical mathematical equations have been derived to express the ground level concentrations of gases downwind from a single source(4, 5). The results of practices which have followed these theoretical considerations agree reasonably well with the experimental work which shows that air contaminants reach their maximum ground concentration at distances of approximately 10 times the stack height. Concentration at that distance varies inversely as the square of the chimney height and its actual value is almost independent of assumptions regarding the variation of diffusion coefficients with height. Thus increasing the height of stacks or increasing the discharge temperature of the gases can be effectively employed in areas not subject to prolonged stagnation periods and light wind movements. Also, dilution of a concentrated source with additional air is sometimes employed. In considering the use of dilution for control purposes, great care must be exercised in determining the weather condi-

TABLE I

Collection Equipment—Solid and Liquid Aerosols

Type	Dust characteristics			Pressure drop, in. H_2O	Advantages	Disadvantages	% Efficiency (wt. basis)	Initial cost, $/c.f.m.
	Type	Particle size, μ	Sp.gr.					
Centrifugal Collectors								
Simple cyclone	Wood dust	50-1,000	0.4-0.7	0.5-2.0	Simple in construction	Low efficiency	70-90	0.55-0.90
	Grain dust	10-200	0.9-1.1				60-80	
	Mineral dust	10-500	2.0-3.0				70-90	
	Pulverized chemicals	10-500	1.5-3.0				70-90	
High-efficiency cyclone	Catalyst dust	2-80	1.5-3.5	2.0-6.0	Relatively high efficiency	Subject to abrasion damage	65-80	
	Fly ash	0.1-100	0.4-1.5				50-70	0.75-1.10
	Other fine dust	5-200	1.0-3.0				85-98	
Impeller	Foundry dust	10-300	2.5-4.0	Acts as own fan	Low space requirement	Impeller abrasion, causing unbalance	70-90	0.75-1.10
Electrostatic Precipitators								
Single-stage	Gray iron Cupola fume	0.5-50	3-6	0.25-0.5	High efficiency under severe conditions	High initial cost, operating difficulties	90-97	1.50-5.00
	Electric steel Furnace fume	0.1-20	5-7				90-97	
	Open hearth steel(a) Furnace fume	0.1-3	5-7				96-99	
	Catalyst dust	2-80	1.5-3.5				85-98	
Two-stage	Oil mist	10-400	∼1	0.25-0.5	High efficiency for low dust loading, safe in operation	Limited in use	85-99	0.90-1.50
	Air conditioning	0.2-10	—	—			95-99	
Cloth Filters								
Tubular	Metallurgical fume			0.5-6.0	High efficiency over wide particle size range	Caking from moisture		0.80-2.50
	Nonferrous	0.03-1.0	∼5				98-99.5	
	Ferrous	0.10-50.0	3-6				97-99.5	
Screen or frame	Ceramic dusts	1-50	1-3	0.5-4.0	Somewhat self-cleaning	Higher stresses on filter mediums	95-99.0	0.80-2.50
	Metallurgical fume	0.1-50	3.6				94-97	
Reverse flow (standard cloths)	Same as screen type shown above			0.5-3.0	Higher dust loadings possible	— —	— —	1.00-2.50
Reverse jet (felt mediums)	Carbon black	0.1-10	1.5	1.0-6.0	Higher filter ratios possible	Bag wear	99.5	1.00-2.00
	Flour dust	5-100	0.9				99.5	
Wet Collectors								
Spray chamber	Rock dust	40-500	2-3	0.5-1.0	Low pressure drop	High nozzle pressure required for good collection	60-75	0.35-1.50
	Asphalt mist	10-400	∼1				70-80	
	Acid mist	20-500	1.1-1.3				70-90	
Inertial	Al and Mg Grinding dust	50-1,000	1.7-2.8	2.0-4.0	No nozzle maintenance	Higher pressure drop	80-95	0.50-1.50
	Foundry dust	10-300	2.5-4.0				70-90	
Centrifugal spray	Rock and sand Dust	20-500	2-3	1.0-4.0	Combined scrubbing and centrifugal action	Abrasion	75-95	0.50-1.50
	Acid and caustic mist	20-500	1.1-1.3				75-95	
Venturi scrubber	Sulfuric acid Mist from concentrator	2-10	∼1.5	10.0-15.0	High efficiency, low water rate	High power consumption	85-95	1.50-5.00
	Chemical fume	0.1-50	1.5-3.5				60-85	

(a) Cold metal furnaces.

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(3) Rose, A. H., Jr., "Control Equipment," Atmospheric Purification Institute, Los Angeles, Calif., 1952. Air Pollution Control District, County of Los Angeles, Publication No. 38.

(4) Bosanquet, C. H., and Pearson, J. L., "The Spread of Smoke and Gas from Chimneys," *Trans. Faraday Soc.*, **32**, 1249 (1936).

(5) Sutton, O. G., "Micrometeorology," McGraw-Hill, New York, 1953.

tions and a clear definition of the effects that are to be removed must be ascertained.

Efforts to solve air pollution problems have been successful at smelters and at other large establishments. Nuisances have been corrected and crop damage eliminated by discharging the gases at high temperatures or by increasing the height of the stack. The results of these changes in several instances have been carefully evaluated by field studies following the modifications. A case in point is illustrated by studies of a smelter where damaging effects of sulfur dioxide were eliminated by raising the stack from 146 ft. to 645 ft.(6). Air measurements made on the existing short stack showed concentrations of 0.5 ppm. for 30 min. recording periods made 842 times during a 7 mo. period. After installation of the high stack, only 1 recording of 0.5 ppm. concentration was reached during a 15-mo. period.

In applying these principles, care must be exercised in considering the effects that are to be eliminated. As an example, dirt precipitated from large particles in many types of processes cannot be markedly reduced by the application of this dilution method. On the other hand, many odor problems and single stack nuisances can be effectively eliminated. The combination of dilution and operational control can be applied under certain conditions where adverse winds or inversions occur at infrequent intervals. When the predetermined threshold values, above which harmful effects will develop are approached, operations of the responsible sources are shut down. Automatic recording equipment is necessary to provide the data for control by this method.

Planning

The principles employed in city plannin and currently applied through zoning restrictions are directed toward the best utilization of the land within a community. Residential areas, industrial zones and essential services are at least theoretically developed and located as to protect property values and to minimize nuisances. As congestion increases and cities approach the population saturation point a multitude of public problems is presented. In the foreground of the complexities of modern civilization is an increasing demand for clean air. The benefits of city planning have been demonstrated in the last decade. Zoning plans could do much to prevent the development of the many nuisances associated with atmospheric pollution.

TABLE II

Classification of Control Devices for Gases and Vapors

Control method	Contaminants	Sources	Remarks.
Absorbers (scrubbers)			
Packed towers	Malodors	Rendering plants, chemical plants, etc.	Absorption solution: oxidizing agents.
Plate towers	Hydrocarbons	Oil refineries	Absorption solution: absorption oil. (Oil is stripped and recirculated.)
Spray towers	Acid Gases		
Spray chambers Water jets	H_2S	Thermal and catalytic cracking plants	Absorption solution: ethanolamines, potassium phosphate, Thylox, sodium phenolate, etc. (The solutions are regenerated.)
	SO_2	Flue gases, chemical plants	Absorption solution: NaOH, $(NH_4)_2SO_3$-NH_4HSO_3, water, alkaline solution. (Chemicals must be replenished.) Dimethylamine (regenerated).
	HNO_3	Chemical plants	Absorption solution: alkaline solution.
Incineration			
Flares	Hydrocarbons	Oil fields, refineries	Venturi burners or steam injection required for smokeless combustion.
Fume burners	H_2S	Oil refineries, chemical plants	SO_2 is product of combustion.
	Malodors	Rendering plants, refineries, chemical plants, paint manufacturing, food processing, etc.	Temperature required 900-1200°F.
Catalytic combustion	Organic vapors	Litho and enameling ovens, rubber compounding, plastics, etc.	Catalysts: platinum, nickel. Temperature required 500°F.
	CO, oil vapors, NH_3	Catalytic cracking unit regenerators	
Adsorption	Organic solvents Malodors	As above As above	Mediums: activated charcoal, silica gel, activated alumina. Mediums regenerated by heat and stripping; disposal of liberated odors, etc., by incineration or other means.
Vapor recovery systems	Gasoline, crude oil, and other volatiles	Storage tanks	Vapors may be compressed and liquefied or may be burned as fuel or flared.
Floating roofs[a]	Gasoline, crude oil, and other volatiles	Storage tanks	

[a] A floating roof is a cover on a vertical cylindrical type of tank which rests on the surface of the liquid within the tank and moves as the level of the liquid changes.

Planning for the location of a single industrial plant should take into account the nature of pollution from the source, potential effects on the adjoining areas, weather conditions and the degree of control that can be applied to the process. Techniques for evaluating these items are available(7, 8). Such advanced planning in growing areas can avoid costly control measures, improve public relations and prevent litigation.

The application of air pollution control zoning or planning on an area basis or to a variety of sources in an area is an extremely complex problem. The need is apparent, however, when consideration is given to the demand that will be placed on science to safeguard the public as the use in industry of radioactive material increases.

The basic consideration is to determine the acceptable level of contamination over an area. The land then should be occupied by a density of sources/acre to keep within the acceptable mass concentration of pollution/acre. Detailed meteorological studies of air currents, diffusion characteristics of the contami-

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(6) Thomas, M. D., Hill, G. R., and Abersold, J. N., "Dispersion of Gases from Tall Stacks," *Ind. Eng. Chem.*, **41**, 2409 (1949).

(7) Holmes, N., "Meteorology," Chpt. 8 in Air-Pollution Abatement Manual, Manufacturing Chemist's Association, Washington, D. C., 1952.

(8) "Effect of Sulfur Dioxide on Vegetation," National Research Council of Canada, Ottawa, Assoc. Committee, 1939.

Measurement of the Visibility Aspect of Air Pollution by Means of Light Scatterings*

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The purpose of this paper is to emphasize how scattered sunlight reduces visibility, and how this scattering can be accurately measured. A reliable means of standardizing this measurement by means of the scattering of air is now available so that this measurement should now be given more consideration. Many light scattering instruments have been used before, but only recently has the idea of an air standard been introduced (1, 2). Sinclair(3) has given an excellent treatment of the basic physics of light scattering and has pointed out its relation to visibility. The instrument described by him was either used to give qualitative results or it could be calibrated with the atmospheric aerosols found in a given locality by passing the atmosphere through a filter and then weighing. The use of a reproducible measurement means that this aspect of air pollution can be reliably measured in a city over a period of many years or that measurements made by different instruments in different cities can be compared.

A common example of light scattering by air pollutants is seen when a searchlight is pointed at the sky at night. This beam is visible largely because of the aerosols present. During the day, the sun is in effect a gigantic searchlight. The sunlight scattered by the polluted air reaches the eyes along with the light from the object viewed. This scattered light interferes very seriously with vision in some cities.

The dirt on a windshield of a car is not very bothersome when driving in the shade or at night when there are no oncoming automobiles. However, bright light on the dirty windshield can practically ruin the visibility of the driver. This pollution on the windshield simulates a dirty atmosphere. Very little light from the object viewed is lost by passing through a dirty windshield. The important effect is the interference due to the light scattered from the strong sunlight or oncoming automobile headlights.

Another point brought up by the foregoing example is that the visibility aspects of air pollution are manifested primarily during bright days when there is strong light to be reflected by the aerosols. This effect is commonly called "haze." On cloudy days and at night this effect is minimized.

The word "haze" needs some clarification. For example, a typical sentence might read, "The smoke and haze of the city are very bad." The word smoke probably should have been omitted because it was the smoke and sunlight combined, or haze, which was observed. Webster's Collegiate Dictionary defines haze as follows: "light vapor or smoke in the air impeding vision." A suggested definition is: sunlight reflected from smoke in the air, which impedes vision.

The author is engaged in developing light scattering instruments for air pollution studies. Fig. 1 illustrates one model which has been developed. It is an arrangement of an automobile headlight viewed at a right angle by a photocell. This differs from several recent instruments which essentially view the light from a forward angle(1, 3). There are two primary reasons for developing the right angle instrument. One is that it simulates the effect produced at noon when the sun is overhead and a person is looking at the horizon. The forward angle scattering instrument would correspond to an observer looking into the sun in the early morning or late evening. The right angle measurement was chosen since it seems to be more representative of actual conditions of vision.

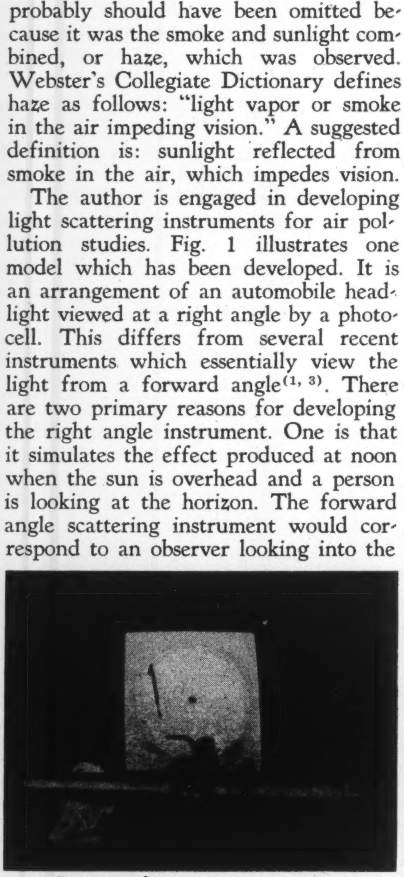
Fig. 1. Light scattering instrument

Another important advantage of the right angle over the forward angle instrument is that stray light can be considerably reduced. The stray light in the instrument shown in Fig. 1 can be reduced to about 1/100 of the light scattered by air. A forward scattering instrument, developed by the author, had stray light about 30 times the light scattered by air.

Meteorologists have long recognized the influence of haze on visibility. Many methods are used to measure visibility. Probably the most common is to note the distance at which objects can just be seen. These results are naturally very dependent on the observer. Thus, they are not very satisfactory in observing the long-term trend in the improvement of the visibility of the atmosphere of a city. Also, visibility cannot be compared between cities because of different conditions of observation. The method of using air as a standard should overcome many of these disadvantages. It is likely, however, that the method of observation will remain important for local use. It does not seem probable that the readings of the instrument can be easily converted to the actual visibility. It is likely that the readings could be interpreted in terms of visibility on a cloudless day at noon in a very flat land area. Thus, this instrument will only measure the visibility aspect of the air for certain fixed conditions, but it will do this very reliably and hence improvements in the atmosphere can be followed over long periods of time.

It is important to emphasize that there is practically no correlation between the haze measured by this instrument and the dirt or grit which is collected in cans. These two types of measurements are totally different. Hemeon, Haines, and Ide(4) have given strong experimental evidence on this point. They have done this by means of optical measurement on filter paper

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(1) Gucker, F. T., Jr., and Peterson, A. H., "A Comparison Photometer to Measure Light Scattering of Aerosols and Gases, Using the Latter as Light-Scattering Standards," *J. Colloid Sci.*, 10, 12 (Feb. 1955).

(2) Gucker, F. T., Jr., Chpt. 75 in "Air Pollution" (McCabe, L. ed.), pp. 620-22, McGraw-Hill, New York, 1952.

(3) Sinclair, D., "Light Scattering Instruments as an Aid in Air Pollution Measurements," *Air Repair*, 3, 51-56 (Aug. 1953).

*Presented at the 48th Annual Meeting of the Air Pollution Control Association at Detroit, Michigan, May 22-26, 1955.

(4) Hemeon, W. C. L., Haines, G. F., Jr., and Ide, H. M., "Determination of Haze and Smoke Concentrations by Filter Paper Samplers," *Air Repair*, 3, 22-28 (Aug. 1953).

An Approach to Odor Control*

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There is an increasing need due to the trend to suburban living and increasing industrialization for effective counteraction of industrial malodors. We are referring, of course, to malodorous emissions which are not of a toxic nature and which have been treated to remove a maximum of particulate matter. Beneficial use is currently being obtained by many industries through the application of deodorants.

We do not propose to review in this paper odor control methods in general because this was done as recently as last year by Amos Turk(1) at the odor symposium before the A.S.T.M. With reference to odor counteraction Dr. Turk states, "The general method has the important practical advantages of low initial equipment costs, negligible space requirements and greater freedom from the necessity of confining the atmosphere into a closed space for treatment." Odor counteraction is the reduction of psychological odor intensity of a malodorous vapor by the nonreactive admixture with other gases or vapors.

We propose to discuss here only our technique for odor counteraction. The first question encountered, "Is it necessary to obtain a sample of the malodorous effluent?" raises the following points.

Many odor nuisances fall into a very similar pattern for similar operations in the same industry. For example, the odors from a sulfate paper pulp mill, from an asphalt blowing operation, from a rendering plant, from a poultry processing plant or from a sewage disposal plant, to name only a few, are all very characteristic. In many cases where we know the basic character of the operation, it is not necessary to secure a sample of the effluent in order to establish its exact nature or to develop a suitable odor reducing agent.

Quite often, however, we meet malodorous effluents which are new to us. For example, in the canning industry the unused parts of many vegetables are piled into stacks at the cannery and the fermenting juices which are collected in lagoons develop unpredictable stenches depending on the particular vegetable.

When working with liquid effluents, it is, of course, a simple matter to collect a sample of the discharge. With vapor effluents we have the alternative of personal study by an experienced observer or collection of the sample.

Personal observation is not always possible because of the unfavorable plume and weather conditions or because of the expense involved. The 2 methods which we employ for sampling are: (1) absorption with a liquid; (2) adsorption with a porous substance.

Collection by Absorption

For the absorption method we use a suction pump to bubble the effluent through portable bottles. Tap water is the collecting liquid. This device can be employed not only to collect the malodor, but also provides a constant check on the efficiency of the odor neutralizer under test. We have used this method at rendering plants with short 30 to 60 ft. stacks. Within minutes of atomizing the odor counteractant into the base of the stack, the odor collected in the gas bottle changes from a stench to a virtually odorless product. A convenient field technique is to use the vacuum from an automobile engine to collect effluent through a Greenburg-Smith Impinger.

Collection by Adsorption

The method of sampling atmospheres for odor by activated carbon adsorption is adapted from similar methods of sampling for gases and vapors described by Turk and co-workers(2). A typical sampling equipment draws air at high volume (50-60 cfm.) through a bed of granular activated carbon arranged in cylindrical canisters to assure even apportionment of air to all parts of the carbon. Sampling must be continued until a sufficient quantity of organic material has been adsorbed for collection, but not until the carbon passes the saturation point.

A sampling unit may be used in an outdoor odorous atmosphere, or may be placed in an enclosure into which a known aliquot of stack gas or process effluent is led. After sampling has been stopped, the carbon is removed, and it may then be used to provide information of 2 types: (a) the results of quantitative steam desorption may be used to calculate quantities of organic material in the vapor sample; (b) desorption of the carbon can provide a representative sample of the odorous material to be used as a basis for specifying odor counteractants mixtures.

The organic material desorbed from the carbon should duplicate the sampled air stream in odor. Superheated steam cannot be used for desorption because of the hydrolytic and other odor-changing reactions which it causes. For removal of representative samples from activated carbon, Turk has used high vacuum desorption with low temperature trapping; this method has been applied to sampling of some vapors of physiological and odor interest in food storage(3).

Example

Although no studies have been made to validate the method of activated carbon sampling and vacuum desorption into cold traps for odor, this appears to be the most promising application of any adsorption method. To illustrate the procedure:

Problem—Malodor from a large stack from a steel plant operation.

Activated carbon sampling—
Contents of sampler: 3 lb. of activated carbon.
Air delivery from a stack: 9.3 cfm. at atmospheric pressure.
Duration of sampling: 144 hr.

Desorption with superheated steam and separate moisture analysis showed that the carbon was saturated to the extent of 13.5% of its original weight with non-aqueous matter.

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(1) A Turk, "Odor Control Methods: A Critical Review," *A.S.T.M. Special Technical Publ.* No. 164, 69 (1954).

* Presented at the 48th Annual Meeting of the Air Pollution Control Association at Detroit, Michigan, May 23-26, 1955.

(2) (a) A. Turk, P. Messer and H. Sleik, "Determination of Gaseous Air Pollution by Carbon Adsorption," *Am. Ind. Hyg. Assn. Quart.* 13, 23 (1952).
(b) A.S.T.M. Committee D-22, "Atmospheric Sampling and Analysis," Tentative Standard Test Procedure on "Analysis of Odors," in preparation.
(c) A. Turk, "Odorous Atmospheric Gases and Vapors: Properties, Collection and Analysis," *Annals N. Y. Acad. Sci.* **58**, Art. 2, 193 (1954).

(3) A. Turk and P. Messer, "Green Lemon Mold. Gaseous Emanation Products," *J. Agric. Food Chem.* 1, 264 (1953).

The carbon was desorbed in vacuo at a pressure of 1-5 μ and the released vapors were passed through the 3 traps held, successively, at temperatures of -10°C. (ice-salt), -80°C. (dry ice), and a final trap also at -80°C. The ice-salt trap held much of the water and some inorganic acids; most of the characteristic organic odorant was obtained in the first dry-ice trap. This material had a mixed sulfide-mercaptan odor, with added pungency due to the presence of sulfur dioxide.

Quantitative Calculation

Using the formula[(4)]:

$$C_W = \frac{1.67\ (10)^4\ SW}{eQ_rt}, \text{ where}$$

C_W = Concentration of odorous vapor (1 lb./10^6 ft.^{3})
S = Degree of saturation of carbon (fractional) = 0.135
W = Weight of carbon = 3 lbs.
Q_r = Rate of air flow through sampler = 9.3 cfm.
t = Time of sampling = 144 hrs.
e = Efficiency of sorbtion = 9.95 (approx.)

then C_W =

$$\frac{1.67(10)^4 \times 0.135 \times 3}{0.95 \times 9.3 \times 144} = 5.3 \text{ lb./million ft.}^3$$

To convert this to concentration in ppm. by volume, we must take an assumed average molecular weight (100 will be in the correct range) and substitute in the formula:

$$C_v = 386 \frac{C_W}{M}$$

$$= 386 \frac{5.3}{100}$$

$$= 20 \text{ ppm.}$$

These quantitative results provide a rational basis for specifying the quantities of odor counteractant needed for a given stack effluent or odorous atmosphere.

Counteractant Specification

The collected odorant samples were used for formulation of counteractants by the following methods:

(a) Malodor — counteractant mixtures were tested on blotter strips until satisfactory odor control was verified by trained experts.

(b) Infrared testing of extracted and dried sample using double beam infrared spectrophotometer Perkins and Elmer Model 21. The procedure used was:

The sample was extracted with 3 cc. of carbon tetrachloride by shaking the mixture in a separatory funnel, continually for 5 min. The mixture was then allowed to stand for 15 min. during which time small bubbles of H_2O were removed from the carbon tetrachloride layer with a stirring rod. The first few drops of carbon tetrachloride were discarded and the remainder was run in a .500 mm. cell without calcium chloride drying. Pure carbon tetrachloride was again used in the reference beam. Spectrum No. 553-28C is representative of this run. It shows principally strong absorption due to SO_2.

(c) A new method which we have used has made it possible to reconstruct the odorous atmosphere in a room into which trained experts can enter. The advantages of an odor test room for subjective evaluations have been reported by several groups of workers in this field[(5)]. The collected odorant, or a known aliquot of it, may be charged into an aerosol bomb and released into an odor-free room. By knowing the volume of the test room, and specifying the volume of the original odorous atmosphere represented by the odorant placed in the bomb, it is possible to odorize the experimental space so as to duplicate the odor of the sampled atmosphere.

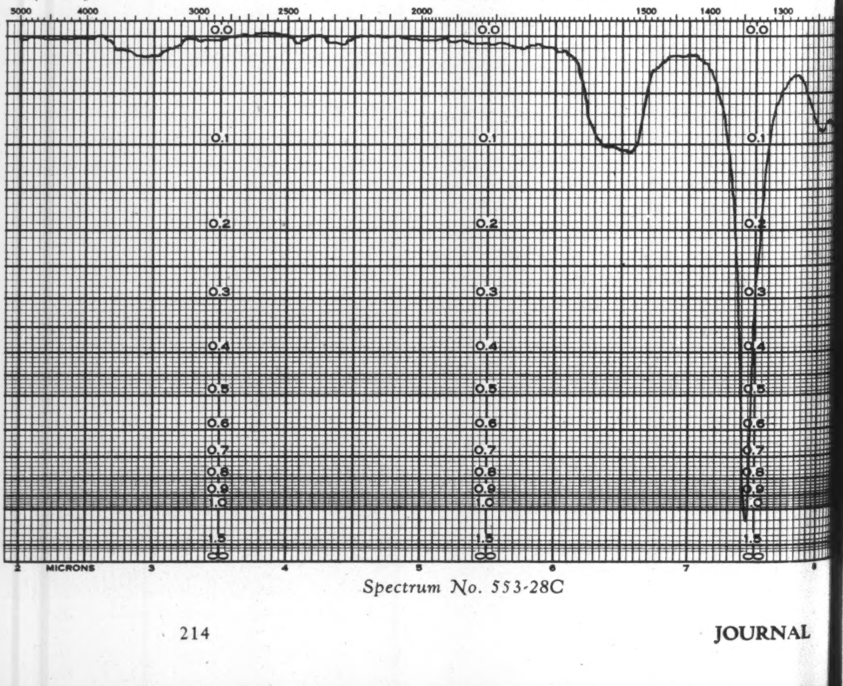
We have built up a library of aerosolized malodors. This includes:

- Phenyl Ethyl Mercaptan
- Furfuryl Mercaptan
- Thioanisole
- Dl Methionine
- Hexahydrobenzoic Acid
- Valeric Acid
- Trimethyl Amine
- Choline
- 3 Acetyl Pyridine
- Oil of Onion
- Benzene Hexachloride
- Skatole
- Dioxane
- Salicylaldehyde
- Triethyl Orthoacetate
- Orthodichlorobenzene
- Cresylic Acid

We have aerosolized and evaluated many candidates as odor counteractants. Products tested have included surface active agents, non-surface active sulfonates, chelate-type oxygen absorbent compounds, sulfamates, aldehydes, ketones, olefins, conjugated diolefins and acetylenes.

The results of any tests on odor counteraction made in this way are then directly applicable to the original problem. In the case of the steel mill effluent, it was found that 0.5 to 1 ppm. of a particular counteractant was required for satisfactory odor control. This is in process of being proved on a commercial basis at this time.

When a high percentage of water vapor occurs in the effluent, water dilutions are applicable in developing the proper deodorant and in checking the ultimate results. We have at our disposal thousands of individual chemical odor-



Spectrum No. 553-28C

[(4)] A. Turk, et al., "Determination of Gaseous Air Pollution by Carbon Adsorption," *Am. Ind. Hyg. Assoc. Quart.* **13**, 23 (1952).

[(5)] Deninger-McKinley, "Design, Construction and Use of an Odor Test Room," *A.S.T.M. Special Publ.* No. 164, 23 (1954).

ants and essential oils with vastly different odor intensities and odor qualities. Table I lists aqueous odor intensity in increasing order for a few individual products(6).

TABLE I
PRACTICAL AQUEOUS ODOR INTENSITY

Odorant	Parts Odorant	Odorant	Parts Odorant
2-Ethyl hexanol	1000	Musk Xylol	100
Benzophenone	900	Isobornyl acetate	50
Diethyl fumarate	900	Methyl anthranilate	10
Phenyl ethyl alcohol	600	Methyl benzoate	10
Cedrenol	600	Citronella, oil of	10
Terpineol	400	p-Cresyl acetate	10
Benzyl propionate	300	Heptaldehyde	1
Anisic Aldehyde	200	Indole	1
Methyl ionone	100	Ethylundecylate	1
Coumarin	100	Methyl heptyne carbonate	0.1

Collection by Condensation

Another promising collection method for odorous gases is collection by condensation(7).

There are a number of apparent advantages to this method. First the collected odorous material is immediately available for further separation without requiring the removal of solvents or desorption from an adsorbent. Second, condensation is the most reliable method for preserving the odorants without chemical reaction with any part of the collecting device or among themselves. The actual techniques for field sampling, however, require bulky and fragile equipment, and detailed attention by a trained operator. We have not used collection by condensation preferring the other methods mentioned above.

Application of Counteractants

There are some odoriferous manufacturing processes which can be treated by adding the odor control agent along with the other reagents. The kraft sulfate and the flax pulping processes can be essentially duplicated in the laboratory. This has 2 advantages in that the malodor can be freshly prepared when required and the counteractant can be experimentally developed and its efficiency proved. Both of these processes are basically an alkaline hydrolysis under reducing conditions. The odor counteractants have to be stable during these severe reaction conditions. Our screening test comprises a $\frac{1}{2}$-hr. cook with 6% sodium hydroxide and 1% sodium sulfide under reflux conditions. The deodorants which have passed this test successfully are then tested for stability in a pressure cook at 150°C. for 3 hr. We use a hydrogenation bomb with a standard rocker arm for agitation. The final deodorant blend is tested in a regular cook in the pressure bomb using wood chips or flax in white liquor. The odor of the charge during blow-off and of the black liquor can be examined under controlled laboratory conditions(8).

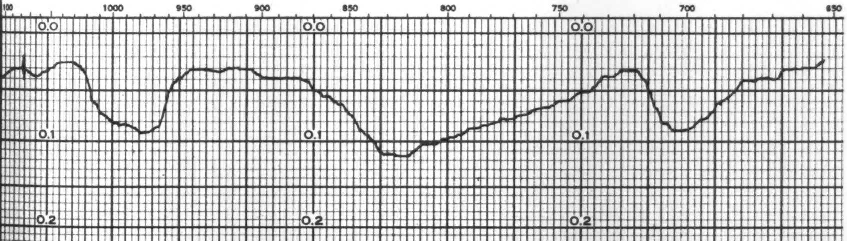
How are our odor neutralizers actually employed in practice? The primary objective is dispersion of the odor counteractant for intimate and continuous admixture with the odoriferous vapors.

Lagoons are simply atomized from the shore line or in some cases the shore line is sprayed with a portable tree sprayer. Normal evaporation under the heat of the sun vaporizes the neutralizer continuously along the entire shore line. This method of application avoids loss of the deodorant by running off with the liquid stream.

For certain processes such as cooking wood chips by the sulfate process or cooking meat scraps and bones in rendering plants, the odor counteractants are added directly to the cook. This is generally done manually although in a few mills, where the expense is warranted, deodorants are added automatically with a proportioning pump. Concentrations normally required are of the order of 10-50 ppm. based on the weight of the charge.

The most widely used application method for an odor counteractant is atomization of a dilute dispersion generally with air. The odor control agent is diluted with water to most practical dilution, normally down to 1-5%; the solution is gravity fed or pumped to a calibrated spray nozzle or jet spray; the injection point is either at the base of the stack or at a point well below the top of the stack to assure good mixing with the effluent vapors.

Odor control agents provide an economical and effective way to make the neighboring plants socially acceptable.



Spectrum No. 553-28C (cont.)

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(6) R. Pantaleoni, "Odors and Fragrances," *Chem. and Eng. News* **31**, 1730-1734 (April 27, 1953).

(7) M. Shepher, S. M. Rock, R. Howard and J. Stormer, "Isolation, Identification and Estimation of Gaseous Pollutants of Air," *Anal. Chem.* **23**, 141 (1951).

(8) W. C. Meuly, B. K. Tremaine, "Abatement of Sulfate Pulp Mill Malodors by Odor Masking Agents," *TAPPI* **36**, No. 4, April (1953).

The Formation of Ozone in Polluted Atmospheres*

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Atmospheric pollution in urban communities which derive their heat and power largely from petroleum products is characterized by the occurrence of unusual concentrations of oxidizing agents during daylight. These oxidizing agents, or oxidants, appear after sunrise and disappear shortly after sunset. A relationship between their appearance and the action of sunlight on atmospheric pollutants has been demonstrated by the fact that they can be produced at night, by irradiating night air with artificial light. These experiments show that the night air contains substances, called "precursors," which can be converted to oxidants by artificial light and, therefore, that the high oxidant levels in the daytime presumably result from such conversion by the radiation of the sun. The origin and mechanism of formation of these oxidants is the subject of this project, supported by the Smoke and Fumes Committee of the American Petroleum Institute.

Although the nature of the oxidants formed by the action of sunlight on pollutants is believed to be complicated, considerable evidence exists to show that much, if not all, of the substance so measured during severe pollution is ozone. Additional contributors to the oxidixing properties of polluted atmospheres are nitrogen dioxide, peroxides, ozonides and, possibly, unidentified substances such as free radicals. In view of the major role of ozone as the oxidant in polluted atmospheres, the emphasis in this study has been on its formation in polluted air in the Los Angeles basin, the present critical area for air pollution.

In any research on polluted atmospheres, the experimenter is dealing with a system in which the manifold variables of nature combine with the variables under his control to produce a very complicated situation. In spite of the obvious drawbacks of dealing with such a complex system, the choice was made to work with the polluted atmospheres of the Los Angeles basin rather than with synthetic atmospheres. Only by working with actual atmospheres will it be possible to be sure that experimental observations are pertinent to what happens rather than to what the experimenter believes happens.

Laboratory Formation of Oxidant From Polluted Air

During the first year of this project a technique was developed for producing an oxidant in polluted air by irradiating the air in a 50-*l.* pyrex flask with 4 H400E-1(1) mercury arcs. As shown diagrammatically in Fig. 1, outside air was drawn at 2.5-*l.*/min. into a 50-*l.* flask, where it had an average residence time of 20 min. The irradiated air was then analyzed by a continuous oxidant recorder which measures, colorimetrically, the iodine formed by the oxidant in a buffered potassium-iodide solution(2). Usually a second oxidant recorder was used to monitor the air stream going to the irradiated flask. The difference in reading between the two instruments was a measure of the oxidant-forming ability of the air. The combination of an irradiated flask and an oxidant recorder has been termed a "precursor system," and the values so obtained have been called "precursor levels." In fact, the readings are the sum of the oxidant formed by irradiation and the oxidant already present, minus any loss of oxidant which has occurred during the residence time in the flask.

Some typical traces of oxidant and precursor levels are shown in Fig. 2 and 3. The precursor level shown in Fig. 2 was high during the night hours and essentially zero during the periods of intense sunlight. The precursor level shown in Fig. 3 was low during the entire day and night. The latter situation existed during much of the 1954 summer period and made experimentation of outside air difficult.

Nature of the Oxidant Precursor

Prior to the occurrence of low precursor levels during the summer, considerable information was obtained on the properties of the oxidant precursor. These experiments were performed by using 3 oxidant recorders. One instrument monitored the oxidant level in outside air. The second measured the precursor level, or the sum of the oxidant which could be formed by irradiating in a flask plus that already present. The third operated as a precursor system except that the air going to the flask was treated by a scrubber, filter, cold trap, etc., to remove, destroy, or modify the precursor. Fig. 4 shows the results of a typical experiment of this type, designed to evaluate the effect of removing acids and nitrogen dioxide with a caustic scrubber. The results of these experiments can be summarized as follows:

1. The formation of oxidant required light with wave lengths below 4,000 Angstrom.
2. The precursor was not seriously affected by reagents designed to remove nitrogen dioxide, organic acids, aldehydes and ketones, organic bases, or particulate material, or by dry-ice-cooled traps.
3. The precursor was removed or destroyed by activated carbon, copper

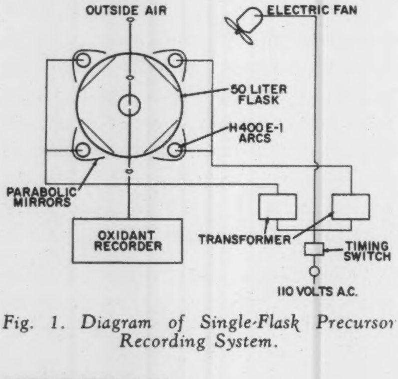

Fig. 1. *Diagram of Single-Flask Precursor Recording System.*

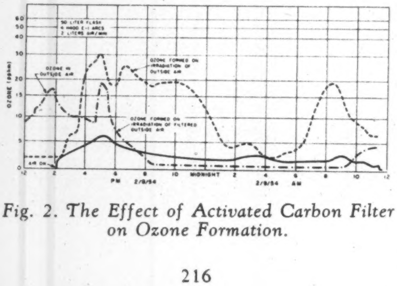

Fig. 2. *The Effect of Activated Carbon Filter on Ozone Formation.*

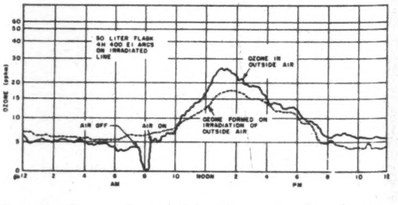

Fig. 3. *Ozone Formed by Constant Irradiation of Outside Air—May 13, 1954.*

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* Presented to a session on smoke and fumes during the 20th Midyear Meeting of the American Petroleum Institute's Division of Refining, in the Jefferson Hotel, St. Louis, Mo., May 10, 1955.

(1) Catalog number of a General Electric mercury vapor lamp which supplies radiation in the range from 3,000 Angstroms to the near infrared.

(2) F. E. Littman and R. W. Benoliel, "Continuous Oxidant Recorder," *Anal. Chem.* **25**, 1480-83 (1953).

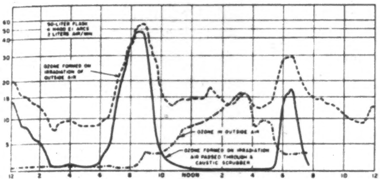

Fig. 4. The Effect of a Caustic Scrubber on Ozone Formation.

oxide at 760 C., or a liquid-oxygen-cooled trap.

4. The precursor removed by a liquid-oxygen-cooled trap could be recovered by warming of the trap, as shown by Fig. 5.

Isolation of the Oxidant Precursor

In view of the apparent exclusion, by these observations, of all known pollutants as the precursor, it was concluded that further progress required the isolation and identification of the constituents of the precursor concentrate obtained in the liquid-oxygen-cooled trap. This objective was concentrated on after the return of precursors after the summer of 1954.

Several features of the precursor isolation and handling procedure required definition. Attention was turned to samples collected by scrubbing night air with 5% sodium hydroxide to reduce the carbon-dioxide level, passing the sample through a dry-ice-cooled trap to reduce the water and oxygenated organics, and then collecting the precursors in a trap chosen from several different designs, illustrated in Fig. 6.

The efficiency of collection and release was measured by allowing the sample collected from a known volume of air to evaporate into a purified stream of air (filtered through activated carbon) flowing into a precursor flask-oxidant recorder system. The efficiency was approximated by comparing the area under the precursor curve during release with the area under the precursor curve during the time of collection.

A representative experiment is shown in Fig. 7, in which the effects of storing collected samples were evaluated. In general, collection and release efficiencies varied from 20 to 75%, and the variations appeared in most cases to be strongly influenced by the nature of the smog during the collection period.

Attempts to use Ascarite in place of 5% sodium hydroxide led to excessive losses of the precursor. The dry-ice-cooled trap had essentially no effect on the precursor level and was used to facilitate the subsequent analytical procedures.

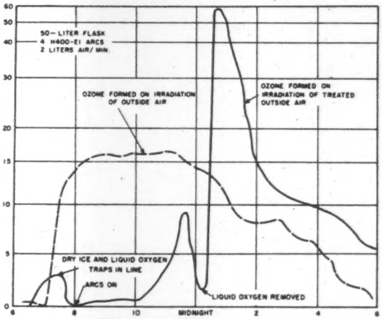

Fig. 5. Liquid Oxygen Cold Trap as a Method for Collecting and Storing Precursors.

Analysis of the Oxidant Precursor

The methods of choice for analyzing the precursor samples were the mass spectrometer and the ultraviolet and infrared spectrophotometers. Major emphasis has been placed on the mass spectrometer, inasmuch as the samples turned out to be very complex. This complexity was not unexpected as the hydrocarbons in polluted air should appear in these samples, with the exception of methane which should pass through the liquid-oxygen-cooled trap.

In order to simplify the interpretation of the spectra, parallel collections were made in which the first sample was taken directly from outside air, and the second sample was irradiated in a precursor flask before collection. It was hoped that the destruction of the precursor by light would permit a comparison of the 2 mass spectra and a fairly simple interpretation. In practice it was found difficult to obtain paired samples whose compositions did not show gross differences in carbon-dioxide and water content. These differences in some of the gross components made comparisons risky.

In general, the mass spectra observed have been characterized as gasoline with the higher molecular weight hydrocarbons reduced in quantity. Chlorinated hydrocarbon fragments are probably present, as are thiophenes and a number of aromatics.

Comparisons of irradiated and non-irradiated samples have shown decreases at masses (m/e) of 43 and 67. Less consistent results have been obtained at masses (m/e) of 15, 26, 37, 39, 55, and 67. Increases were less consistent and appeared usually at masses (m/e) of 13, 29, 31, 57, 72, 91, and 106.

A less specific type of comparison was made by the method of Brown⁽³⁾, in

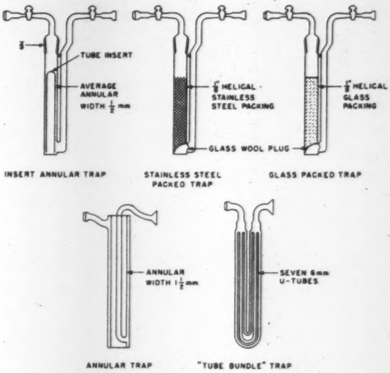
TUBE INSERT
AVERAGE ANNULAR WIDTH $\frac{1}{2}$ mm
$\frac{1}{8}$" HELICAL STAINLESS STEEL PACKING
$\frac{1}{8}$" HELICAL GLASS PACKING
GLASS WOOL PLUG
INSERT ANNULAR TRAP
STAINLESS STEEL PACKED TRAP
GLASS PACKED TRAP
ANNULAR WIDTH 1$\frac{1}{2}$ mm
SEVEN 6mm U-TUBES
ANNULAR TRAP
"TUBE BUNDLE" TRAP

Fig. 6. Precursor Trap Designs.

which the gasoline-type compound is calculated. Some representative results are given in Table 1. The main conclusion to be drawn from these data is that a decrease of CODA (cycloolefines, dienes, and acetylenes) occurred during the irradiation process. It is not clear whether their disappearance was due to reaction with the ozone formed or whether they are related to the formation of the ozone.

Relationship of Nitrogen Oxides to the Precursor

During the program of isolation and identification of the precursor, 2 instruments were being developed to determine continuously the nitrogen-dioxide and nitric-oxide contents of polluted air. Some of the preliminary experiments defining these instruments were performed on this project. These instruments became available about the first month of 1955 and were used to obtain further knowledge of the precursor. As has been so often the case in air-pollution study, a scientific advance was possible when an analytical tool became available.

The nitrogen-dioxide recorder brings a stream of polluted air and a modified Griess reagent⁽⁴⁾ together concurrently in a horizontal helix consisting of 3-mm. ID glass tubing. The nitrogen dioxide forms nitrous acid in the reagent which diazotizes sulfanilic acid followed by

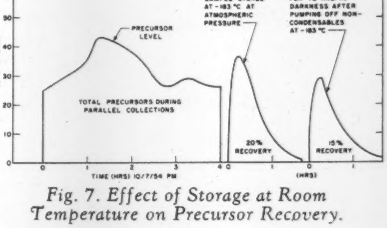

Fig. 7. Effect of Storage at Room Temperature on Precursor Recovery.

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(3) R. A. Brown, "Compound Types in Gasoline by Mass Spectrometer Analysis," *Anal. Chem.* 23, 430-37 (1951).

(4) Bernard E. Saltzman, "Colorimetric Microdetermination of Nitrogen Dioxide in the Atmosphere," *Anal. Chem.* **26**, 12, 1949 (1954).

coupling to N-1-naphthylethylenediamine. The resulting dye is determined colorimetrically. The nitric-oxide recorder is equivalent to the nitrogen-dioxide recorder with the addition of a small stream of ozonized oxygen and a holding chamber to oxidize the nitric oxide to nitrogen dioxide. The only serious interference observed is a response to organic nitrites.

The nitrogen-dioxide recorder was used to monitor the air going to and coming from a precursor flask. From Fig. 8 it is obvious that the irradiation process produced nitrogen dioxide, and possibly organic nitrites. Inasmuch as previous results had eliminated nitrogen dioxide as the precursor, the discovery that it was formed by irradiation required a revision of the previous conclusion. The use of the nitric-oxide recorder to monitor polluted air during periods when precursor was present established its probable presence in significant quantities.

Additional evidence was obtained by collecting samples from polluted air when precursors were present and performing experiments to establish the nature of the nitrogen-dioxide-forming material in polluted air.

1. A sample collected in a liquid-oxygen-cooled trap through a dry-ice-cooled trap formed large quantities of nitrogen dioxide and oxidant when released into purified air (activated-carbon filtered) flowing through an irradiated flask.
2. A similar sample formed large quantities of nitrogen dioxide when mixed with ozone, using the nitric-oxide recorder system.

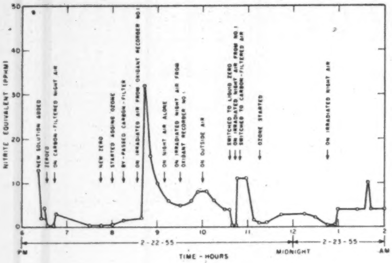

Fig. 8.

3. The nitrogen-dioxide-forming substance was collected in a liquid-oxygen-cooled trap from polluted air which had been filtered through activated carbon. The detection was with the nitric-oxide recorder system.
4. Finally, the properties of nitric oxide from a cylinder were studied by making a mixture with purified air (activated-carbon filtered) and observing its behavior. It was established that nitric oxide passed a dry-ice-cooled trap and an activated carbon filter, was collected by a liquid-oxygen-cooled trap, and could be rapidly converted to nitrogen dioxide by ozone in a nitric-oxide recorder.
5. Finally, the nitrous oxide present in the atmosphere at about 0.5 ppm. is not detected by either the nitrogen-dioxide or the nitric-oxide recorder, and the photolysis of nitrogen dioxide with its accompanying oxygen atoms leaves the nitrous oxide unchanged.

Identification of Nitric Oxide in Polluted Air

Several attempts were made to isolate nitric oxide from the atmosphere so that its presence could be confirmed spectroscopically. These experiments consisted of removing the nitrogen dioxide and carbon dioxide from polluted air by activated carbon and Ascarite, reducing the water by a dry-ice-cooled trap, and collecting in a liquid-oxygen-cooled trap. The condensate was then distilled into an optical cell with sodium-chloride windows. Although the nitrous oxide in the atmosphere was readily detected in this manner, the infrared bands of nitric oxide or the ultraviolet and infrared bands of nitrogen dioxide formed from it by air oxidation have so far not been observed. Evidence of traces of nitrogen dioxide can be inferred from some absorption in the 3,500 Angstrom to 4,000 Angstrom region. This failure can be attributed to the low intensity of the nitric-oxide infrared bands and probable oxidation of nitric oxide in a liquid-oxygen-cooled trap in the presence of air to nitrogen dioxide [5,6]. The presence of water obviously complicates detection of the resulting nitrogen dioxide.

That nitrogen-dioxide-organic-compound mixtures in air can form oxidant at the concentrations and under the irradiation conditions characteristic of sunlight has been confirmed by the use of the precursor system. Nitrogen dioxide was added to purified air obtained by filtration through activated carbon to

(continued on page 246)

TABLE 1
Calculated Results for Gasoline-Type Compounds,[a] **Carbon Dioxide, Air, and Water**

Sample	Analysis, Per Cent by Volume									
	Aliphatic Paraffins		O and CP[b]		CODA[c]		Aromatics	Carbon Dioxide	Air	Water
	1	2	1	2	1	2				
1997-2	7.3	3.2	3.3	7.4	0.76	0.50	1.29	54.7	3.1	29.6
1997-1	1.12	0.62	0.37	1.44	0.12	0.05	0.32	8.8	0.3	88.7
2023-2	0.13	0.04	0.07	0.07	0.01	0.01	0.01	99.5	0.3	0.06
2023-1	0.14	0.06	0.04	0.13	0.01	0.01	0.02	99.5	0.2	0.07
2050-2	3.08	1.37	1.82	3.40	0.49	0.23	0.53	29.5	6.4	58.4
2050-1	1.70	0.75	0.48	1.62	0.11	0.05	0.31	95.7	1.1	0.5
2069-2	0.22	0.05	0.02	0.17	0.03	0.02	0.05	94.9	1.8	3.0
2069-1	0.09	0.04	0.03	0.16	0.01	0.01	0.04	98.3	1.3	0.2
2086-2	2.80	0.32	—0.29	0.96	0.20	0.10	0.13	93.6	1.9	2.2
2086-1	1.50	0.18	—0.13	0.37	0.06	0.08	0.05	95.1	0.9	2.8
Background for 2086	0.07	0.04	0.13	0.20	0.05	0.02	0.03	. . .	0.5	3.2

[a] Gasoline-type compounds were calculated by using the method of R. A. Brown, Anal Chem. 23 480 1951).
[b] O and CP are mono-olefins and cycloparaffins, assuming equal amounts of each.
[c] CODA are cycloolefins, diolefins, and acetylenes.

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[5] F. C. Henriques, Jr., A. B. F. Duncan, and Albert Noyes, Jr., "Photochemical Studies—XXVII: The Effect of Radiation on Mixtures of Nitrogen Dioxide and Nitrous Oxide and Its Relationship to the Photochemical Decomposition of Nitrous Oxide," *J. Chem. Phys.* **6**, 518-22 (1938).

[6] James Younger Macdonald, "The Photochemical Decomposition of Nitrous Oxide and Nitric Oxide," *J. Chem. Soc.* (London) 1-14 (1928).

Reactions Involving Ozone, Nitrogen Dioxide, and Organic Compounds at Low Concentrations in Air†*

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A characteristic feature of the Los Angeles smog is the unusually high concentration of an oxidizing agent which has been measured in the atmosphere during smog attacks. Extensive studies of this oxidant by the Stanford Research Institute and others have indicated that it is probably ozone. Its concentration usually can be correlated closely with the subjective estimate of smog severity.

This correlation suggests that a study of atmospheric reactions involving ozone would lead to a better understanding of smog, even though ozone itself is not believed to be responsible for the unpleasant features of smog. Two important questions need to be answered. First, how is ozone formed in the atmosphere? Second, what part does it play in producing the objectionable features of smog.

Investigations by the Stanford Research Institute(1) have shown that ozone can be produced in polluted air by subjecting it to ultraviolet radiation from mercury arcs. This shows that ozone is produced by a photochemical reaction in the polluted atmosphere and is almost certainly not of meteorological origin. Haagen-Smit(2,3) has presented evidence that ozone is produced when a mixture of nitrogen dioxide with 3-methylheptane in air is subjected to ultraviolet radiation. Analysis of atmospheric samples shows that nitrogen oxides and hydrocarbons, as well as other organic substances, are present in polluted air. In two other papers(4,5) Haagen-Smit suggests that the reaction of ozone with olefins produces substances which are capable of causing damage to crops similar to that found after a smog attack.

Two key reactions, therefore, have been suggested:

(1) the photochemical reaction of nitrogen dioxide with hydrocarbons;

(2) the reactions of ozone with hydrocarbons. It would be desirable to establish with certainty the products and mechanism of these reactions. These are the aims of the study in progress at the Laboratories for Research and Development at The Franklin Institute. Results obtained during the period from June 1, 1953, to February 28, 1955, are reported in this paper.

Experimental Methods

The technique used in the experiments consisted simply of mixing the reactants in air, allowing them to stand with or without ultraviolet irradiation, and then analyzing the products.

Ozone was generated by an electric discharge through oxygen in an ozone generator patterned after that of Henne and Perilstein(6). Iodometric analysis of the ozone-oxygen stream showed that about 4 mole%—6% by weight—was obtained. Extra-dry tank oxygen, prepurified nitrogen, dry carbon-dioxide—free air, and tank nitrogen dioxide were used. The hydrocarbons were Phillips Petroleum Company research grade. Other chemicals were obtained in the highest purity available from chemical suppliers and were used directly.

Fig. 1 is a schematic diagram of the apparatus. A typical experiment, such as an ozone-olefin reaction, was performed as follows: First, all flasks were evacuated. The ozonized oxygen was then trapped in the 500-ml. bulb and expanded into the left-hand 5-*l.* bulb. The other reactant was placed in the right-hand 5-*l.* bulb, and then dry, carbon-dioxide—free air was admitted to both flasks until the pressure reached approximately 1 atm. Next, the gases were alowed to flow together into the third bulb—in which the pressure dropped to ⅔ atm. — where they were allowed to react either with or without ultraviolet irradiation from a carbon arc. Finally the reaction products were expanded into the 1-m. infrared-absorption cell, air was added to the cell until the total pressure reached 1 atm. and the spectrum was run. Pressures of gases were measured with a manometer containing silicone vacuum-pump oil. Especially low pressures were obtained by expanding from measurable pressure in a small flask to the lower pressure in a large flask.

The source of ultraviolet radiation was a carbon arc with "sunlight" carbons operated at about 35 v. and 30 amp. Making allowance for the absorption by the pyrex flask, it was calculated that the radiation which fell on the reactants approximated sunlight both in intensity and spectral distribution in the ultraviolet region.

The analyses were performed with a single-beam, single-pass infrared spectrometer employing a sodium-chloride prism in a Littrow mount and a-c electronics. Infrared analysis is extremely well suited to the problem at hand. For one thing it is a very sensitive technique; *e.g.*, in an absorption cell of 1-m. path

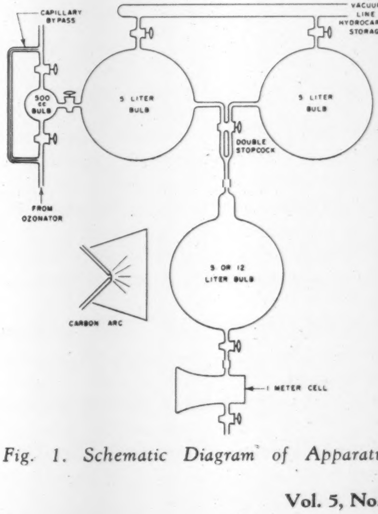

Fig. 1. Schematic Diagram of Apparatus.

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(1) "An Experimental Study of Oxidants and Organics in Urban Atmospheres" *Technical Report No. 5*, Stanford Research Inst., Mar. 31 (1954).

(2) A. J. Haagen-Smit, C. E. Bradley, and M. M. Fox, "Formation of Ozone in Los Angeles Smog," *Natl. Proc. Air Pollution Symposium. 2nd Symposium, Pasadena, Calif. 1952*, 54 (1952).

(3) A. J. Haagen-Smit and M. M. Fox, "Automobile Exhaust and Ozone Formation." paper presented at the SAE Golden Anniversary meeting, Detroit, Mich., Jan. 10-14 (1955).

† Presented to a session on smoke and fumes during the 20th Midyear Meeting of the American Petroleum Institute's Division of Refining, in the Jefferson Hotel, St. Louis, Mo., May 10, 1955.

* This paper constitutes a report on the work carried out under the sponsorship of the American Petroleum Inst., Smoke and Fumes Committee.

(4) A. J. Haagen-Smit, "Chemistry and Physiology of Los Angeles Smog," *Ind. Eng. Chem.* **44**, 1342-6 (1952).

(5) A. J. Haagen-Smit, E. F. Darley, M. Zaitlin, H. Hull, and W. Noble, "Investigation on Injury to Plants from Air Pollution in the Los Angeles Area," *Plant Physiol.* **27**, 18-34 (1952).

(6) A. L. Henne and W. L. Perilstein, "The Preparation of Aldehydes and Ketones by Ozone Oxidation," *J. Am. Chem. Soc.* **65**, 2183 (1943).

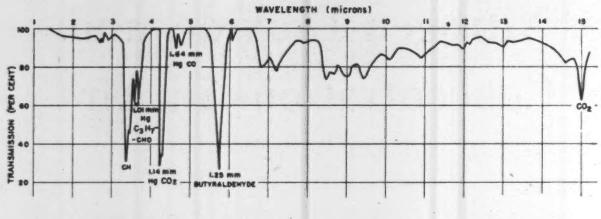

Fig. 2. Infrared Spectrum of Reaction Products—1-Pentene and Ozone, Each at 2.5 Mm. of Mercury; Air at 1 Atm.; 1-M Cell.

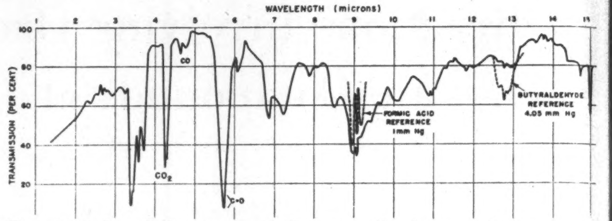

Fig. 3. Infrared Spectrum of Reaction Products—1-Pentene and Ozone, Each at 5.5 Mm. of Mercury; Air at 1 Atm.; Reacted in 1-M Cell.

length, gases at partial pressures on the order of 1 mm. can be detected. Also the results of infrared analysis are usually unequivocal; even members of a homologous series of compounds can be distinguished from one another. Another advantage of infrared analysis over other techniques — *e.g.*, mass spectrometry — is that the system being analyzed is disturbed very little during analysis inasmuch as the infrared radiation does not destroy the substance being detected. Furthermore, a number of components can be determined simultaneously, and reliable quantitative data can be obtained.

Care must be taken when the concentration of an absorber is calculated from the intensity of its infrared bands. There is a pressure-broadening effect in the spectra of certain substances, especially the smaller molecules. This effect makes the infrared absorption very sensitive to total pressure. For this reason all of the spectra obtained in this research were run at a total pressure of 1 atm.

Pressures of reactants given with the illustrations are the pressures which would have existed in the 1-m. cell after expansion from the reaction flask had there been no reaction. The volume of the 1-m. cell is 1 *l.* When the 5-*l.* flask was used for reaction, the actual pressures at which reaction took place were, therefore, six-fifths times the pressures given in the captions to the illustrations.

Reactants which did not react to any appreciable extent in the absence of the carbon-arc irradiation were premixed in the reaction flask, pressurized to 1 atm. with air, and then reaction was begun by turning on the arc. The experiments on the nitrogen-dioxide-olefin reaction, the nitrogen-dioxide-aldehyde reaction, the nitrogen-dioxide-saturated hydrocarbon reaction, and the ozone-saturated hydrocarbon reaction were performed in this way.

The longer the path length of light through the gases, the lower the partial pressure of a gas which can be detected. With a 1-m. path length it is convenient to use partial pressures on the order of a few millimeters of mercury. Therefore, most of the experiments in the present research were done at these pressures. This is about 1,000 times larger than the concentrations normally found in polluted atmospheres. For exploratory work at lower pressures the following technique was devised:

The gases were reacted in a 12-*l.* flask at partial pressures well below the limit for infrared detection in the 1-m. cell. The reactants were mixed with pure oxygen at a pressure of a few centimeters of mercury, instead of with 1 atm. of air. An outlet at one side of the 12-*l.* flask was attached to the evacuated 1-m. absorption cell. At the conclusion of reaction, air was allowed to flow into the 12-*l.* flask from the other side until the total pressure was 1 atm. The air pushed the reaction products before it and compressed them into the 1-m. cell, where they were then at detectable partial pressures. The technique was useful even though there was some mixing of the gases during compression. With the 12-*l.* flask, the 1-m. cell (vol. approx. 1 *l.*) a reaction pressure of 5 cm. of mercury, and a final total pressure (after compression) of 1 atm., the partial pressure of the reaction products was increased approximately sevenfold on compression.

Results and Discussion

Ozone-Olefin Reaction

When mixed at partial pressures of a few millimeters of mercury in an atmosphere of air, ozone and 1-pentene react very rapidly, even without ultraviolet irradiation. A mist appears immediately, but slowly settles out to form a liquid film on the walls of the reaction vessel. The lower the pressures of reactants, the less dense is the mist.

The infrared-absorption spectrum of the products, recorded after expanding them into an evacuated 1-m. cell, shows principally aldehyde, carbon dioxide, and carbon monoxide. Such spectra are reproduced in Fig. 2 and 3. The bands at 3.58 and 3.69 μ are characteristic of aldehyde, but cannot be used to identify the particular aldehyde, inasmuch as most of the lower aldehydes have a very similar structure in this region. However, the band at 12.8 μ distinguishes butyraldehyde from its homologues, and the spectrum of Fig. 3 does show this band. From the 3.69 μ band it is estimated that butyraldehyde represents about ½ of the original pentene. If the carbonyl band—5.75 μ—is assumed to be entirely caused by butyraldehyde, a slightly — about 20 %—higher concentration is calculated. Therefore, other carbonyl compounds are apparently present in small amounts. They are probably formed in the oxidation of the newly formed butyraldehyde in the presence of ozone, as will be discussed later. In a series of experiments in which reactant pressures were successively lowered it was found that the per-cent excess carbonyl absorption remained approximately the same and also that the fraction of pentene converted to aldehyde remained about one-half to two-thirds. The remaining pentene probably was split up among various gaseous products other than the aldehyde, the liquid products, and the unreacted pentene.

The 1-pentene molecule apparently is ruptured at the double bond by ozone attack, the 4-carbon fragment yielding butyraldehyde. The fate of the end-methylene group is uncertain. Reactions at higher pressure produce some formic acid, as shown in Fig. 3, but not enough to account for the end-methylene groups. At a lower pressure (Fig. 2) no formic acid is detectable. No formaldehyde was detected in any of the spectra. However, the formaldehyde infrared bands are relatively weak and are overlapped by the strong CH and carbonyl bands from the other products. Therefore, formaldehyde could not be excluded on the basis of the infrared spectrum alone. The ultraviolet spectrum of formaldehyde is quite characteristic. Accordingly, a sample of the gaseous products of the reaction of 1-pentene at 8.0 mm. of mercury—and ozone at 8.0 mm. of mercury —was transferred to a 10-cm. absorption cell, and the ultraviolet spectrum was recorded with a spectrophotometer. The results are shown in Fig. 4. The comparison spectra in this figure show that formaldehyde at 1 mm. or less of mercury can be detected. No formaldehyde was detectable in the unknown, even though 8.0 mm. pressure would have been produced if each molecule of pentene had produced one of formaldehyde. Ozone does not react very fast with formaldehyde, so the possibility of the formaldehyde being destroyed by ozone as fast as it is formed is ruled out. The fate of the end-methylene group, then, still cannot be established. It probably appears as carbon monoxide and carbon dioxide.

The presence or absence of water vapor in the reactants was not found to affect the ozone-1-pentene reaction; nor was the reaction affected by the light from the "sunshine" carbon arc.

The properties of the mist were studied briefly. Three extra salt windows were mounted inside a 10-cm. gas-absorption cell so that the mist would deposit on them. The ozone and 1-pentene were mixed in the cell, each at partial pressures of 30 mm. of mercury, in the presence of 1 atm. of oxygen. After allowing the mist to settle for 10 min., the gases in the cell were pumped out and replaced with nitrogen. The infrared spectrum which was then recorded did not show any strong absorptions. No specific compounds or groups were identified in this spectrum. The weakness of the infrared absorption obtained in this way makes it probable that the liquid products contribute little or no absorption to the spectra of the gases obtained in the 1-m. cell (such as Fig. 2 and 3).

In another experiment ozone and 1-pentene—each at a partial pressure of 3.5 mm. of mercury in 1 atm. of air—were reacted in a 5-*l*. flask. After the mist had settled for half an hour the gas phase was flushed out with nitrogen, and the oxidizing strength of the liquid products was determined by rinsing the flask with potassium-iodide solution and titrating the iodine which was liberated with sodium thiosulfate. About 2 % of the oxidizing power of the ozone remained in the liquid products.

Attempts were made to detect a transitory ozonide in the reaction mixture and some success was achieved. It is reported that ozonides have infrared absorption bands in the carbonyl region and in the region around 8.3 μ(7). In order to detect these absorptions 1-pentene and ozone were reacted in the spectrometer-absorption cell, with the spectrometer set to record absorption at a single wave length as a function of time. This experiment was repeated at various wave lengths.

At the reactant concentrations used for these experiments—1-pentene and ozone at 0.62 mm. of mercury each, in 1 atm. of air—the reaction is much too fast to permit a detailed study with our equipment. With the spectrometer set at 8.4 μ absorption increased very rapidly when the 2 reactants were mixed in the cell, and then slowly decreased over a period of several minutes. This absorption was still decreasing long after the absorptions at 10.90 μ (pentene), 9.47 μ (ozone), and 4.26 μ (carbon dioxide) had stabilized. This indicates that an unstable intermediate, which absorbs at 8.4μ, is formed and then disappears. This is believed to be the ozonide.

In most of the work thus far described, equal amounts of 1-pentene and ozone were used. One experiment was done with an excess of ozone. In this experiment ozone at 2 mm. of mercury and 1-pentene at 1 mm. of mercury were mixed in 1 atm. of air by the usual procedure. The infrared spectrum was recorded after expanding the products into the 1-m. cell and pressurizing to 1 atm. with air. The most notable new product was peroxy acid, which was identified by its characteristic absorption at 3.05 μ. This is presumably formed by the reaction of excess ozone with the butyraldehyde formed by the initial rapid reaction of 1-pentene with ozone. This is discussed more fully in a later section of this paper.

Nitrogen-Dioxide—Olefin Reaction

Nitrogen dioxide was reacted with the normal 1-olefins from ethylene to 1-pentene, the 1-pentene reaction being studied in detail. No detectable reaction occurred in the dark but, when the gases were irradiated with the light from the "sunshine" carbon arc, reaction products formed. All the 1-olefins gave the same type of major products, viz., carbon dioxide, aldehyde, other carbonyl compounds, and organic nitrogen compounds.

The spectrum of the products of a reaction between nitrogen dioxide and 1-pentene in air is shown by the dotted line in Fig. 5. The strong alkyl-nitrate bands at 6.05 μ, 7. 8 μ, and 11.7 μ appear identical in the spectra of many different alkyl nitrates, and the weaker absorptions in the spectral region of 9.0 to 10.5 μ must be used to distinguish a given nitrate from its isomers and homologues. Interference by other absorbers in this critical region makes identification very difficult, as was the case in Fig. 5. It was necessary to isolate a pure sample of the nitrate to make an exact identification. The procedure was as follows:

(a) the reaction between 1-pentene, and nitrogen dioxide in air was conducted in a 12-*l*. flask at comparatively high pressures (4 cm. of mercury for pentene, 2 cm. of mercury for nitrogen dioxide, and 1 atm. of air);

(b) the products were blown slowly through a tube of ascarite which absorbed acid vapors, including the unreacted nitrogen dioxide;

(c) they were passed through a dry-ice cold trap, which trapped out aldehyde and nitrate;

(d) the aldehyde was extracted from the nitrate with sodium-bisulfite solution;

(e) the nitrate was distilled into the infrared-absorption cell. The spectrum which was recorded is shown by the dotted line in Fig. 6. This spectrum shows conclusively that the compound is propyl nitrate. Fig. 6 shows the spectrum of a sample of propyl nitrate isolated from the products of the reaction between nitrogen dioxide and butyralde-

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(7) E. Briner, B. Susz, and E. Dallwigk, "Recherches sur les Spectres d' Absorption Infrarouges de Ozonides," *Helv. Chim. Acta* 35, 345 (1952).

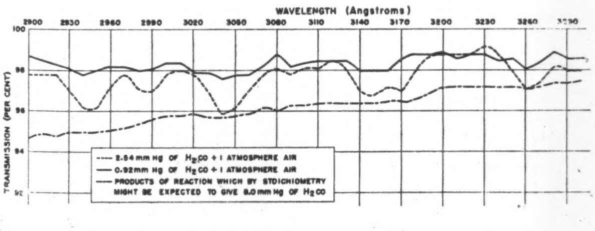

Fig. 4. Ultraviolet Absorption Spectrum of Reaction Products of 1-Pentene and Ozone in Air; with Reference Spectra of Formaldehyde; 10-Cm. Beckman Cell.

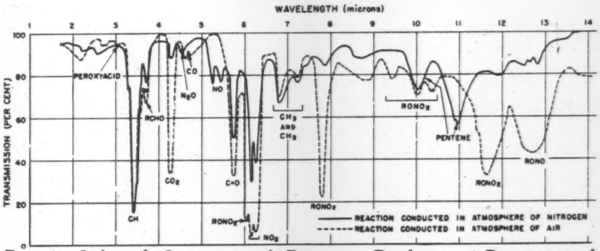

Fig. 5. Infrared Spectrum of Reaction Products—1-Pentene and Nitrogen Dioxide, Each at 2.7 Mm. of Mercury; Irradiated 30 Min.; 1-M Cell.

TABLE 1

Effect of Ultraviolet Filters on 1-Pentene-Nitrogen-Dioxide Reaction

Each Reactant at 2 Mm. of Mercury after Expansion into 1-M. Cell—Irradiated 20 Min.

Product	Wave length (μ)	Amount Formed (Millimeters of Mercury) No Filter	No. 7380[a] (15 Per Cent at 360 Mμ)	No. 3060[a] (3 Per Cent at 400 Mμ)
Carbon dioxide	4.29	0.27	0.11	0.04
Carbon monoxide	4.62	0.42	0.43	...
Butyraldehyde	3.70	0.61	0.41	...
Carbonyl (as butyraldehyde)	5.74	1.21	0.98	0.23
Alkyl nitrate	7.79	0.092	0.05	...

[a] Corning identification number and transmission; molded filters were used.

hyde. This is discussed hereinafter. The sample isolated from the products of the nitrogen-dioxide and 1-pentene reactions shows a larger absorption at several wave lengths, particularly 3.4 μ. This is probably caused by some 1-pentene remaining in the purified sample. Alkyl nitrite does not appear in Fig. 6 because little or none is formed at the high concentrations of 1-pentene and nitrogen dioxide used for this preparation.

The presence of alkyl nitrite among the products of the 1-pentene-nitrogen-dioxide reaction is indicated by the absorption band in Fig. 5 at 12.7 μ. A second strong band of alkyl nitrite falls in the region of 6.0 to 6.2 μ. Both alkyl nitrate and nitrogen dioxide absorb strongly in this region, as shown in Fig. 5.

Other bands in Fig. 5 are the aldehyde C-H band at 3.69 μ, the carbonyl band at 5.75 μ, the carbon-dioxide band at 4.28 μ, and the carbon-monoxide band at 4.66 μ. It was not possible to decide which particular aldehyde was formed on the basis of the details of its spectrum because there was too much interference from the spectra of other products. However, there is evidence (to be discussed later) that the propyl nitrate is formed from the reaction between the aldehyde and nitrogen dioxide and, inasmuch as the butyraldehyde-nitrogen-dioxide reaction is found to give propyl nitrate, it is concluded that the aldehyde formed from 1-pentene and nitrogen dioxide is butyraldehyde (see Fig. 6).

The fate of the end-methylene group of the 1-pentene has not been established. No formic acid or formaldehyde was ever detected in these spectra.

The small peak at 3.05 μ in Fig. 5 is caused by peroxy acid. This is an important product, as will presently be pointed out.

An estimate of the fraction of reactants converted to products in a typical reaction can be obtained by reference to the column headed "No Filter" in Table 1. Experiments performed at low pressures using an excess of pentene over nitrogen dioxide—*e.g.*, a tenfold excess—have produced 3 or more times as many aldehyde molecules as there were nitrogen-dioxide molecules to start. Roughly speaking, longer irradiation gives a greater per-cent conversion of reactants to products although, of course, a limit is approached. This point has not been investigated in detail.

The effect of molecular oxygen on the photochemical reaction can be seen by comparison of the solid and dotted lines of Fig. 5. No organic nitrogen compounds were formed in the absence of oxygen, although aldehyde was formed. The decrease in the amount of aldehyde formed when the reaction was carried out in nitrogen rather than air may have resulted from the fact that a smaller amount of nitrogen dioxide was available for photolysis. The spectrum showed that only about ⅓ of the nitrogen dioxide remained at the end of the reaction; the rest was probably nitric oxide.

The fact that the reaction in nitrogen did produce a substantial amount of aldehyde indicates that oxygen atoms from the photo dissociation of nitrogen dioxide attack the olefin directly, rather than first reacting with molecular oxygen to produce ozone.

To test the effectiveness of various regions of the ultraviolet spectrum in activating the nitrogen-dioxide-pentene reaction in air, the reactants were irradiated through various filters. The results given in Table 1, show that the amount or reaction gradually increased as shorter wave lengths were included.

A clear-cut statement cannot be made as to the exact wave-length limit for photochemical reaction because of the gradual cutoff of the filters and the gradual increase in the amount of reaction.

Ozone—Saturated-Hydrocarbons Reaction

The reactions between ozone and saturated hydrocarbons at partial pressures in the millimeter range in air have been examined briefly. When not irradiated, these reactions are very slow. When exposed to ultraviolet radiation from the carbon arc, reaction occurs more rapidly, but still much slower than the reaction between olefins and ozone. The experiments were done with 2-methylpentane, *n*hexane, and cyclohexane. The amounts of carbon-dioxide and carbonyl absorption produced indicate that 2-methylpentane is somewhat more reactive to ozone and *n*hexane, and *n*hexane is somewhat more reactive than cyclohexane. The infrared spectrum of the products of the ozone-2-methylpentane reaction is shown in Fig. 7. The carbonyl band at 7.78 μ is prominent. The only other identifiable products are carbon dioxide and acetone. The acetone almost certainly arises from the branched end of the molecule, following attack at the tertiary hydrogen atom. The fate of the remaining 3-carbon fragment is not apparent from the infrared spectrum

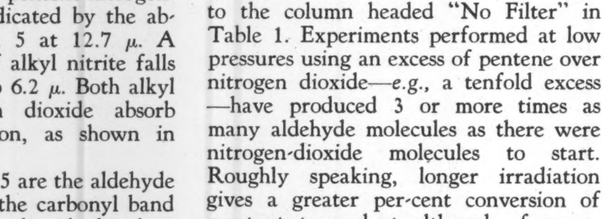

Fig. 6. Infrared Spectrum of Propyl Nitrate Isolated from Reaction Products — Dotted Line Represents Products of Reaction of 1-Pentene at 4 Cm. of Mercury, Nitrogen Dioxide at 2 Cm. of Mercury, and Oxygen at 1 Atm.; Irradiated 30 Min.; 1-M Cell. Solid Line Represents Product of Reaction of Butyraldehyde and Nitrogen Dioxide, Each at 2 Cm. of Mercury, and Oxygen at 1 Atm.; Irradiated 30 Min.; 1-M Cell.

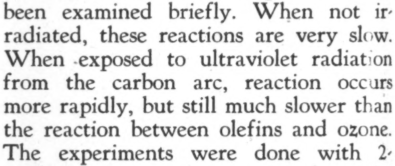

Fig. 7. Infrared Spectrum of Reaction Products—2-Methylpentane and Ozone, Each at 1.5 Mm. of Mercury; Air at 1 Atm.; Irradiated 1 Hour; 1-M Cell.

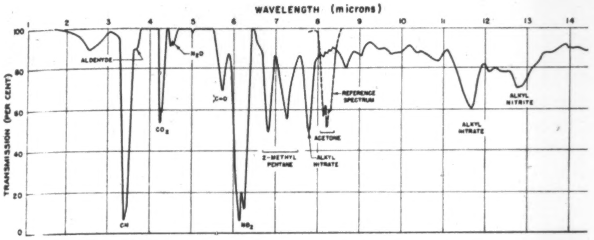

Fig. 8. *Infrared Spectrum of Reaction Products—2-Methylpentane and Ozone, Each at 1.5 Mm. of Mercury; Air at 1 Atm.; Irradiated 1 Hour; 1-M Cell.*

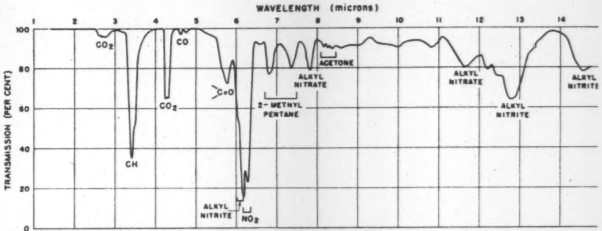

Fig. 9. Infrared Spectrum of Reaction Products—2-Methylpentane and Nitrogen Dioxide, Each at 0.21 Mm. of Mercury, and Oxygen at 80 Mm. of Mercury; Irradiated 1 Hour; Products Compressed into 1-M Cell with Oxygen until Pressure was 1 Atm.

of the products. It may be oxidized to aliphatic acid—thus accounting for some of the carbonyl absorption—or it may be completely oxidized to carbon dioxide and water. Acetone was not detected as a product of the *n*hexane or cyclohexane reactions. The lack of characteristic bands at 3.58 and 3.68 μ indicate that little or no aldehyde is present. Considerable amounts of ozone and hydrocarbon remain unreacted even after 1 hr. of irradiation. In a separate experiment ozone—at 0.90 mm. of mercury—in air was exposed to the radiation from the carbon arc for ½ hour, and it was found that, within the experimental error, none had decomposed during irradiation. In similar experiments with hydrocarbon present an appreciable fraction of the ozone disappeared.

The mechanism by which the light induces reaction between saturated hydrocarbons and ozone is obscure. It does not seem possible that the hydrocarbons are the light absorbers, inasmuch as they are transparent to the wave lengths used. Ozone does absorb in the spectral region concerned. However, this absorption does not cause ozone to disappear when it is mixed only with pure oxygen. Why, then, will it disappear with an accompanying reaction when saturated hydrocarbons are present? Three possible explanations are:

(1) ozone is activated by the light, and then reacts with hydrocarbons;

(2) ozone dissociates under the light, but forms again unless there is hydrocarbon present to react with oxygen atoms;

(3) radicals or molecules are present from a slight "dark" reaction, and they are the light absorbers which promote photochemical reaction. Further work will be needed to clarify this point.

Nitrogen-Dioxide—Saturated-Hydrocarbons Reaction

Nitrogen dioxide and saturated hydrocarbons at pressures in the millimeter range in air were found to react to a measurable extent only when they were irradiated with the "sunshine" carbon arc. The reactions were much slower than the analogous reaction between nitrogen dioxide and olefins. The chief products were carbon dioxide, carbonyl compounds, organic nitrates, and organic nitrites. The experiments were done with 2-methylpentane, *n*hexane, and cyclohexane. The 2-methylpentane — nitrogen-dioxide reaction and the *n*hexane-nitrogen-dioxide reaction each produced about the same amount of products. However, the cyclohexane-nitrogen-dioxide reaction produced less.

The 2-methylpentane-nitrogen-dioxide reaction was studied in the most detail, and Fig. 8 and 9 are the spectra of the products of 2 of these experiments. A carbonyl compound, organic nitrate, organic nitrite, carbon dioxide, and acetone can be identified. When Fig. 8 and 9 are compared, it can be seen that the percentage of reactants converted to products in a given time was not reduced when the pressures of reactants were sharply cut down. On the contrary, the percentage conversion was increased. Also to be noted is the fact that at the lower pressure organic nitrite formed in preference to organic nitrate, whereas at higher pressures the nitrate predominated. The lowest pressures at which 2-methylpentane and nitrogen dioxide were reacted were with each reactant at 0.04 mm. of mercury in oxygen at 80 mm. of mercury. They were irradiated for 1 hr., after which they were compressed into the meter cell (see section on experimental methods).

The detection of acetone as a product indicates that the attack takes place at the tertiary hydrogen of the 2-methylpentane. The remaining 3-carbon fragment may form aldehyde which is oxidized further to form the organic nitrates and nitrites observed in the product spectrum. This is supported by the observation that molecular oxygen is necessary for the formation of nitrite and nitrate from 2-methylpentane. Molecular oxygen is also necessary for the oxidation of aldehyde, by irradiated nitrogen dioxide, to peroxy acids and organic nitrite and nitrate (discussed later).

Ozone-Aldehyde Reaction

Because butyraldehyde appeared as a major product of the ozone-pentene reaction, an investigation of the reaction between butyraldehyde and ozone was undertaken. In contrast to the ozone-pentene reaction, the reaction of butyraldehyde with ozone is slow. After butyraldehyde and ozone, both at 1.4 mm. of mercury, were mixed with 1 atm. of air and allowed to stand, the products were transferred to the 1-m. cell, and the spectrum was recorded. This spectrum is shown in Fig. 10. The essentially complete reaction of ozone is shown by the absence of the characteristic ozone bands at 9.59 μ. The aldehyde bands at 3.58 and 3.68 μ indicate that some unreacted butyraldehyde is present. The carbonyl absorption at 5.7 μ indicates that, in addition to unreacted butyraldehyde, there is a substantial amount of other carbonyl compounds. It is notable that carbon monoxide is absent, whereas carbon dioxide is quite strong. Three bands not observed in the spectrum of the ozone-pentene products are prominent in this spectrum. These are at 3.05 μ, 6.88 μ, and 8.53 μ in Fig. 10. It was suspected that these bands resulted from peroxybutyric acid and, therefore, a reference sample of peroxybutyric acid was prepared(8). Its spectrum is shown in Fig. 11. The peroxy acid was found to decompose in the vapor phase, its half life being on the order of ½ hr. The spectrum of the decomposition products is also shown in the figure. These products were primarily aliphatic acid and carbon dioxide. This spectrum resembles butyric acid more closely than propionic acid, although it is obvious that a peroxybutyric-acid molecule which decomposes to give carbon dioxide cannot also give butyric acid. It may be that 2 modes of decomposition are involved, with the carbon dioxide arising from a small portion of the peroxy acid. The spectra confirmed our expectation that peroxybutyric acid was formed in the ozone-butyraldehyde-air reaction. A sample of peroxypro-

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(8) F. G. Fischer, H. Dill, and S. L. Volz, "Uber die Einwirkung von Ozon auf Aldehyd," *Ann Chem. Justus Liebigs* **486**, 80 (1951).

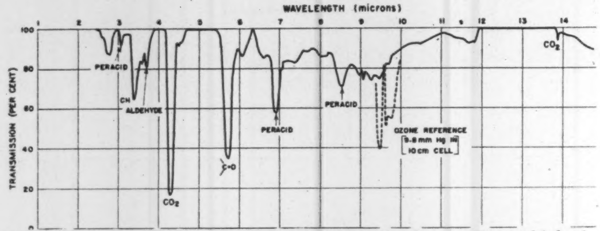


Fig. 10. *Infrared Spectrum of Reaction Products—Butyraldehyde and Ozone, Each at 1.4 Mm. of Mercury; Air at 1 Atm.; 1-M Cell.*

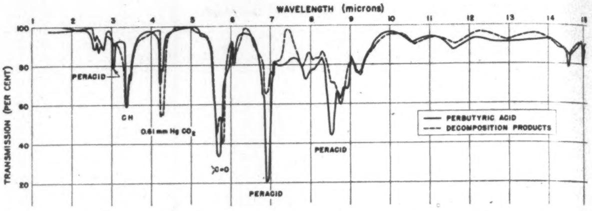


Fig. 11. *Infrared Spectrum of Peroxybutyric Acid and Its Decomposition Products—Peroxy Acid at 3.96 Mm. of Mercury, Air at 1 Atm.; 1-M Cell.*

pionic acid was prepared by a procedure similar to that used for peroxybutyric acid. Its infrared spectrum also showed the bands at 3.05 μ, 6.88 μ, and 8.53 μ. It is somewhat more stable than peroxybutyric acid.

The experiments which gave Fig. 10—butyraldehyde and ozone, each at 1.4 mm. of mercury, in air—was repeated, and the products—mostly gaseous, but containing some liquid formed as a mist—remaining in the reaction flask were treated with potassium-iodide solution to determine oxidizing agents. Titration of this solution showed that about 21% of the oxidizing power of the original ozone was present. A partial spectrum of the gaseous products before and after treatment with potassium-iodide solution is shown in Fig. 12. It can be seen that the potassium-iodide solution removes peroxy acid and ozone but not formic acid.

In another experiment, butyraldehyde—at 6.6 mm. of mercury—was pressurized with air to 1 atm., and exposed to the carbon-arc irradiation for 2 hr. without added ozone. Again the 3 peroxy-acid bands—3.05 μ, 6.90 μ, and 8.53 μ—were apparent. Treatment of the products remaining in the reaction flask with potassium-iodide solution, followed by titration with thiosulfate, showed that oxidizing power had been formed equivalent to a 9% conversion of the butyraldehyde to peroxybutyric acid. The photochemical oxidation of aldehyde was found to be much slower than the ozone oxidation. It was also found that the ozone-aldehyde reaction proceeds at about the same rate whether there is irradiation or not.

TABLE 2

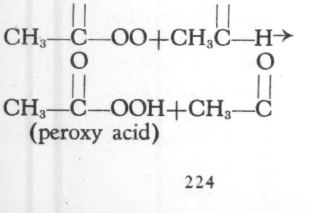
Relative Amounts of Peroxy Acid Produced by Reaction of Ozone with Various

Aldehyde	Absorption, at 3.05 Microns (Per Cent)
Formaldehyde	0.0
Acetaldehyde	1.6
Propionaldehyde	3.7
Butyraldehyde	4.5
Valeraldehyde	2.5
Hexaldehyde	1.9
Heptaldehyde	1.4

The presence of molecular oxygen was found to be necessary for the production of peroxy acid in the ozone-aldehyde reaction. Ozone was isolated by condensing it in a liquid-nitrogen trap and pumping off all oxygen. The oxygen was replaced with pure nitrogen, the ozone was allowed to revaporize, and then this ozone-nitrogen mixture was reacted with aldehyde. The peroxy acid was produced only very slowly. Peroxy acid was produced much more rapidly in an experiment in which the oxygen was not completely removed from the condensed ozone.

Tests were made to see how much peroxy acid is produced in the reaction of various aldehydes with ozone. Each of several aldehydes at a partial pressure of 0.8 mm. of mercury was mixed with ozone, at 0.8 mm. of mercury, in 1 atm. of air and irradiated for 20 min., after which the spectrum of the gases was taken to determine how much absorption there was at the characteristic 3.05 μ band of peroxy acids. The results are given in Table 2.

A paper was recently presented⁽⁹⁾ in which it was argued that the low-temperature oxidation of acetaldehyde takes place by the following chain mechanism:



$$\mathrm{CH_3{-}\overset{\overset{O}{\|}}{C}{-}H + O_2 \rightarrow CH_3{-}\overset{\overset{O}{\|}}{C} + HO_2} \qquad (1)$$

$$\mathrm{CH_3{-}\overset{\overset{O}{\|}}{C} + O_2 \rightarrow CH_3{-}\overset{\overset{O}{\|}}{C}{-}O{-}O} \qquad (2)$$

$$\mathrm{CH_3{-}\overset{\overset{O}{\|}}{C}{-}OO + CH_3\overset{\overset{O}{\|}}{C}{-}H \rightarrow}$$

$$\underset{\text{(peroxy acid)}}{\mathrm{CH_3{-}\overset{\overset{O}{\|}}{C}{-}OOH}} \mathrm{+ CH_3{-}\overset{\overset{O}{\|}}{C}} \qquad (3)$$

The terminating step of the chain was given as the mutual destruction of two radicals.

The results of the present experiments support this chain mechanism. No reaction was observed between aldehyde and air at room temperature in the dark but, when the mixture was irradiated with the "sunshine" carbon arc, when nitrogen dioxide or biacetyl was added and irradiated, or when ozone was added, the formation of peroxy acid was observed. In other words, O_2 in equation (1) was replaced at various times by light quanta, oxygen atoms, acetyl radicals, or ozone molecules. The role of molecular oxygen in the chain reaction—equation (2) — is supported by the fact that, in the *absence* of O_2, very little peroxy acid is formed when aldehyde is reacted with ozone or with irradiated nitrogen dioxide.

Nitrogen-Dioxide—Aldehyde Reaction

Nitrogen dioxide and aldehyde were found to react to air when irradiated with the "sunshine" carbon arc. They did not react in the absence of irradiation. Peroxy acid, alkyl nitrate, and alkyl nitrite were products of the reaction. A sample of the nitrate formed in the re-

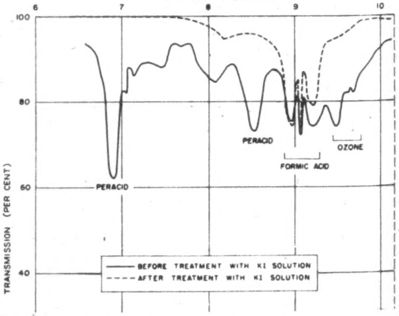


Fig. 12. *Infrared Spectrum of Reaction Products—Butyraldehyde and Ozone, Each at 1.4 Mm. of Mercury; Air at 1 Atm.; Reacted 2 Hours; 1-M Cell.*

⁽⁹⁾ C. A. McDowell and J. B. Farmer, "The Kinetics of the Thermal and Photochemical Oxidation of Acetaldehyde," paper no. 15 presented at the Fifth Symposium (International) on Combustion, Pittsburgh, Pa., Sept. (1954).

action of butyraldehyde and nitrogen dioxide was isolated by the same procedure used to separate this compound from the products of the nitrogen-dioxide—1-pentene reaction. Its spectrum is shown in Fig. 6 (solid line). The spectrum shows the compound to be propyl nitrate[10]. Experiments show that, as the partial pressure of the reactants is lowered, alkyl nitrate becomes a more important product. At the lowest partial pressures used in the present work—butyraldehyde at 0.06 mm. of mercury, nitrogen dioxide at 0.03 mm. of mercury in 1 atm. of air, irradiated 30 min.—more nitrite than nitrate was formed. This experiment was done by the pressurization technique described in the section on experimental methods. This is the same observation which was made when the 1-pentene and nitrogen-dioxide reaction was studied.

Neither peroxy acid nor organic nitrogen compounds were formed when butyraldehyde and nitrogen dioxide were mixed with pure nitrogen and irradiated.

Peroxy-Acid—Nitrogen-Dioxide Reaction

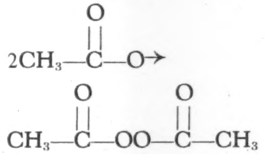
Propyl nitrite was found to be the major product of the reaction between peroxybutyric acid and nitrogen dioxide when this mixture was allowed to react in air without irradiation. Some propyl nitrate also was formed. When the mixture was irradiated, much more propyl nitrate was formed than before, perhaps by photolysis of propyl nitrite. In separate experiments it was found that photolysis of butyl nitrite does yield nitrate as well as other products. Butyl nitrate is not photolyzed by "sunlight" irradiation. Propyl nitrite and propyl nitrate were formed when peroxybutyric acid and nitrogen dioxide were reacted in the presence of pure nitrogen.

Inasmuch as aliphatic acids are prominent contaminants of the peroxy acids, it might be suspected that the alkyl nitrate and alkyl nitrite might arise from reaction of these simple acids with nitrogen dioxide. This is not the case because a mixture of butyric acid and nitrogen dioxide in air failed to produce a detectable amount of nitrate even after 45 min. of "sunlight" irradiation.

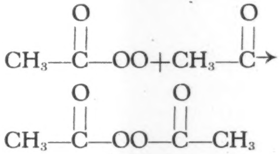
The fact that peroxy acid and nitrogen dioxide produce alkyl nitrate and alkyl nitrite even when reacted in nitrogen may be significant. It stands in contrast to the formation of alkyl nitrate from either the nitrogen-dioxide—1-pentene reaction or the nitrogen-dioxide—aldehyde reaction, both of which require molecular oxygen for the formation of alkyl nitrate. It may mean that in these last 2 reactions alkyl nitrate and alkyl nitrite are formed via the peroxy acid. Decomposition of the peroxy acid by the splitting out of carbon dioxide would result in the formation of propyl radicals which might then react with nitrogen dioxide to give the nitrite.

Biacetyl-Aldehyde-Air Reaction

When irradiated with the carbon arc, biacetyl was found to promote the oxidation of acetaldehyde in air to peroxyacetic acid. No reaction took place in the absence of irradiation. Biacetyl peroxide was detected as a product of this reaction. It probably arose from one of the following recombination reactions:



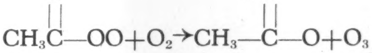
$$2CH_3{-}\overset{O}{\overset{\|}{C}}{-}O\rightarrow CH_3{-}\overset{O}{\overset{\|}{C}}{-}OO{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \qquad (4)$$



$$CH_3{-}\overset{O}{\overset{\|}{C}}{-}OO+CH_3{-}\overset{O}{\overset{\|}{C}}\rightarrow CH_3{-}\overset{O}{\overset{\|}{C}}{-}OO{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \qquad (5)$$

Photolysis of biacetyl alone in air produced a much smaller amount of this peroxide, but no ozone was detected. Experiments showed that ozone was destroyed when it was mixed with biacetyl and the mixture irradiated. Neither biacetyl peroxide nor ozone decomposed when irradiated alone.

It has been suggested that the peroxyacetyl radical may react with molecular oxygen to form ozone:



$$CH_3\overset{O}{\overset{\|}{C}}{-}OO+O_2\rightarrow CH_3{-}\overset{O}{\overset{\|}{C}}{-}O+O_3 \qquad (6)$$

This reaction would be in competition with the reaction in equation (3); i.e., aldehyde and molecular oxygen would compete for the peroxy-acetyl radicals. Higher concentrations of aldehyde in air would favor the reaction in equation (3) and the production of peroxy acid. However, at much lower concentrations of aldehyde the reaction in equation (3) is slowed down relative to the reaction in equation (6). Thus peroxy acid may be the major oxidizer formed at higher concentrations, and ozone may become the important product at low concentrations. Thus ozone may be produced by aldehyde oxidation in the atmosphere even though it is not detectable in our experiments at much higher concentrations.

Summary and Conclusions

The reaction between ozone and 1-olefins in air at room temperature produces an aldehyde of one less carbon atom than the olefin, in addition to other products. The aldehyde is apparently preceded by a transitory ozonide. This rapid reaction also produces a mist of liquid products. "Sunlight" irradiation does not affect the reaction. An excess of ozone leads to further oxidation of the product aldehyde to acid and peroxy acid.

When a mixture of nitrogen dioxide and 1-olefin in air is subjected to artificial-sunlight irradiation, a reaction occurs to produce an aldehyde of one less carbon atom than the parent 1-olefin. Oxidation of this aldehyde leads to the corresponding aliphatic acid, the peroxy acid, alkyl nitrate, and alkyl nitrite. These last 2 compounds have one less carbon atom than the aldehyde. Molecular oxygen is involved in the reaction leading to acid, peroxy acid, nitrate, and nitrite, but not in the reaction leading to aldehyde.

Ozone and saturated hydrocarbons in air are caused to react to a slight extent by "sunlight" irradiation. The identifiable products are a carbonyl compound, carbon dioxide and, in the case of 2-methylpentane, acetone. 2-Methylpentane is more reactive than *n*hexane which, in turn, is more reactive than cyclohexane. The mechanism of this photochemical reaction has not been established, inasmuch as neither hydrocarbon nor ozone alone is decomposed by "sunlight" irradiation.

The photochemical reaction of nitrogen dioxide with saturated hydrocarbons is slower than the corresponding reaction with 1-olefin. Organic nitrate, organic nitrite, carbon dioxide, and a carbonyl compound are produced. The reaction of nitrogen dioxide with 2-methylpentane also produces acetone. Neither alkyl nitrate nor alkyl nitrite is formed when this reaction is conducted in nitrogen instead of air.

Low concentrations of reactants favor the formation of alkyl nitrite rather than alkyl nitrate when either 1-pentane or 2-methylpentane is reacted with nitrogen dioxide under "sunlight" irradiation.

The reaction of ozone with aldehyde in air produces peroxy acid. The ozone acts as an initiator of the oxidation of aldehyde because very little peroxy acid

(continued on page 244)

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[10] For reference spectra see: J. B. Levy and F. J. Adrian, "Kinetic Study of the Thermal Decomposition of Some Organic Nitrates: II—n-Propyl Nitrate and t-Butyl Nitrate," *NAVORD Rept. 2608*, U. S. Naval Ordnance Laboratory, White Oak, Md.

Isokinetic Flow and Sampling*

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The sampling of airborne particulates by chemists, physicists, biologists, meteorologists, engineers, and investigators in the field of medicine is indicative of the many types of aerosol sampling being performed. Some of the investigators engaged in this field of sampling realize the importance of isokinetic sampling but are unfamiliar with the errors incurred by deviation from isokinetic conditions, others are confused by it, and it is completely overlooked by others.

Isokinetic conditions prevail when there is no divergence of flow lines around the sampler inlet. The velocities of the sampled and sampling streams must be equal, and the sampler must face directly into the sampled stream in order to minimize or eliminate divergence of the flow lines at the sampler inlet. When divergence of these flow lines is present there is the possibility of particle size fractionation. Many investigators[1] have contributed to the practices now being used in isokinetic sampling.

Familiarity with isokinetic flow and sampling is necessary when determining the performance of sampling instruments, when evaluating aerosol and air pollution data, and when obtaining information for the design of sampling equipment.

Obtaining a representative aerosol sample, often a primary factor in the intelligent selection of an aerosol dispersing apparatus or collecting device, is usually very difficult and subject to many errors. Special precautions must be taken when sampling to avoid segregation or classification of the particulate material. When the sampling velocity is too low, *i.e.*, the velocity in the sample tube is less than the velocity in the main stream, the particles in the stream will enter the sampling tube due to their greater inertia while the gas is diverted around the tube. This gives a higher particulate concentration in the sample tube than in the main stream, as illustrated in Fig. 1a. Similarly, if the sampling velocity is too high, *i.e.*, the velocity in the sample tube is greater than the velocity in the main stream, the inertia of the particle will keep the particle from following the flow lines which converge into the sampling tube. This gives a lower concentration in the sampling tube than in the main stream, as illustrated in Fig. 1b. A finer particulate sample is obtained where the sampling velocity is too high and a coarser particulate sample when the velocity is too low.

The location of the sampling tube in a system is an important part of the sampling operation. Usually samples should be taken at various points across a tube to obtain a representative sample. It is interesting to observe the velocity profile across a tube, as shown in Fig. 2. The reduced velocity at the edges of the tube is due to friction, roughness of surface, and turbulence. One of the best sampling points in a system is at the end of a long straight vertical section of tubing. Long horizontal tubing tends to yield a higher and coarser particulate concentration near the bottom of the tube. However, in sampling from a vertical tube it is well to keep in mind that all particles in the tube may not be moving at a uniform rate and that the larger particles may be moving only along the tube axis. It is often desirable when conveying large particles to use a high degree of turbulence. Also, it is obvious that the shorter the tube length the lower the loss of particulate material on the tube walls. Bends will tend to concentrate the particulate material at the outside walls of the tubing. It is often a good idea to install a mixing device, such as a disk baffle or nozzle, in the tubing some distance upstream from the sampling location.

When attempting to obtain a truly representative sample of air-borne particulate material, the following points should be considered:

1. Velocity balancing of the main and sampling streams. (For minimum divergence of flow lines these velocities must be equal. A sharp edge on the sampling inlet aids in reducing divergence and turbulence.)
2. Position of the sampling inlet relative to that of the main stream. (Divergence of lines of flow is minimized: when the sampling inlet faces directly into the main stream.)
3. Length of the sampling tube. (Tube losses are reduced by using a shorter sampling tube.)
4. Diameter of the sampling inlet. (Investigations have shown that the improper selection of an appropriate sampling tube diameter is a source of error[2]).
5. Particle size distribution and density of the material. (These factors aid in estimation of the inertial effects of the airborne particulate material).

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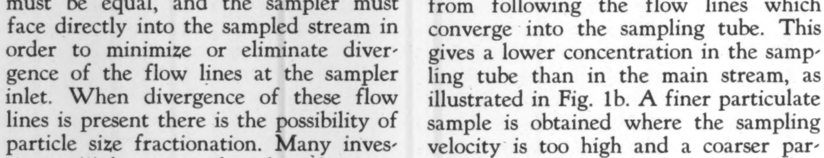

Fig. 1 (a)

Fig. 1 (b)

Fig. 1. The inertial effects of particles are shown resulting in non-isokinetic sampling. The flow lines depict non-isokinetic flow. The large hollow spheres represent particles of a relatively large mass, and the small solid spheres represent particles of a relatively small mass.

(a) The sampling velocity is too low, the large particles in the stream enter the sample tube due to their greater inertia while the small particles and the gas follow the flow lines.

(b) The sampling velocity is too high, the inertia of the large particles will keep them from following the flow lines which converge into the sampling tube.

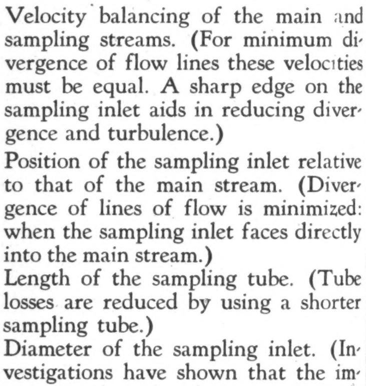

Fig. 2. Velocity profile across a tube. The reduced velocity at the edges of the tube is due to friction, roughness of surface, and turbulence.

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*Presented at the Conference on the Physics of Cloud and Precipitation Particles at Woods Hole, Mass., Sept. 7-10, 1955.

The Concentration of Ozone in the Atmosphere of Certain American Cities

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The undesirable effects of the pollution of the atmosphere in the Los Angeles area have been attributed to organic materials and their oxidation products. The troublesome compounds are believed to result from the reaction of hydrocarbons with nitrogen dioxide and other oxidants which have been found in appreciable concentration in the atmosphere in association with low-lying haze[1,2]. Under such conditions concentrations of oxidant as high as 80 pphm. have been found and levels between 20 pphm. and 50 pphm. are of frequent occurrence, in contrast to less than 5 pphm. when the atmosphere is clear[1,2]. Data provided by continuous recorders have shown that the peak concentration of oxidant occurs approximately at midday, after which there is a progressive decrease which reaches its lowest level during the night[1,3]. This suggests that the formation of the oxidant is the result of a photochemical reaction. The cracking of bent rubber strips and selective adsorption-desorption techniques have been used in order to demonstrate that the oxidant present in the air is principally ozone[2,4].

These chemical characteristics of the atmosphere in the Los Angeles area have not been noted elsewhere, it appears. This fact, coupled with the apparently unique type and severity of the human response (lacrimation) to the polluted atmosphere of the area, has seemed to justify an investigation of the levels of concentration of ozone (or oxidant, as it will be referred to hereinafter) in other American cities. The investigation is being sponsored by the Smoke and Fumes Committee of the American Petroleum Institute and has been in progress for approximately 2 yr., during which time tests have been made in 10 American cities. The results of the analytical survey for the first year have been reported [5] and, therefore, this paper will review these findings briefly and describe in detail the progress which has been made since they appeared.

Method of Analysis

Inasmuch as the data were to be compared with those obtained in Los Angeles, the method which was employed to determine the oxidant in other cities was the same as that used there. The analytical method and the instrument, which have been described elsewhere, depend on the automatic measurement and recording of the quantities of iodine released when air containing an oxidant is passed through a solution of potassium iodide buffered to pH 7[6]. Iodometric methods lack specificity, and although the interference of both nitrogen dioxide and sulfur dioxide were considered to be insignificant factors in the determinations made in the Los Angeles area, it was believed that they would have to be accounted for in the eastern section of the country where sulfur-containing coal is burned in large quantities. Laboratory tests with mixtures of ozone and sulfur dioxide indicated that sulfur dioxide decreased the instrumental recording of the concentration of the oxidant by approximately one part for each 3 parts of sulfur dioxide[7]. This response does not agree with the expected stoichiometric reaction between sulfur dioxide and iodine and, therefore, the interference is believed to occur in the scrubber of the instrument and to be expressed best by the following equation:

$$3\,SO_2 + O_3 + 3\,H_2O \rightarrow 3\,H_2SO_4 \qquad (1)$$

If the concentration of sulfur dioxide is sufficient, the recorder can be expected to indicate zero concentrations of oxidant, and many such tracings were obtained in field tests. Fig. 1 is representative of the type of tracing which was obtained (in Elizabeth, N. J.) when a high concentration of sulfur dioxide was present in the air. Fig. 2 is a tracing obtained on a clear, mild day in the same city when the concentration of sulfur dioxide was low. The levels of con-

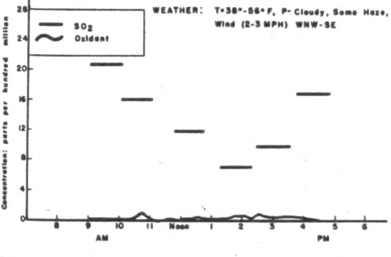

Fig. 1. The Concentration of Oxidant Indicated by the Recorder during a Day in Elizabeth, N. J., When the Concentration of Sulfur Dioxide was High.

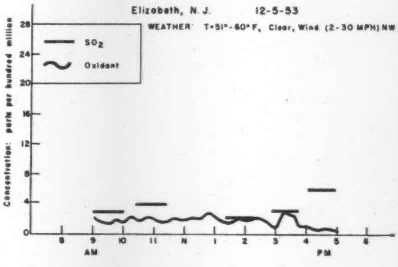

Fig. 2. The Concentration of Oxidant Indicated by the Recorder during a Day in Elizabeth, N. J., When the Concentration of Sulfur Dioxide Was Low.

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(1) *The Smog Problem in Los Angeles County, Los Angeles, Calif.*, a report prepared by the Stanford Research Inst. for the Western Oil and Gas Assoc. (1954).

(2) A. J. Haagen-Smit and M. M. Fox, "Photochemical Ozone Formation with Hydrocarbons and Automobile Exhaust," *Air Repair* 4, 105 (1954).

(3) A. J. Haagen-Smit, "The Control of Air Pollution in Los Angeles," *Eng. and Sci.*, Dec. (1954).

Presented to a session on smoke and fumes during the 20th Midyear Meeting of the American-Petroleum Institute's Division of Refining, in the Jefferson Hotel, St. Louis, Mo., May 10, 1955.

(4) *Ozone in the Lower Atmosphere*, Stanford Research Inst. Project No. C-844, Technical Report No. 1, prepared for the American Petroleum Inst., Sept. (1953).

(5) *The Concentrations of Oxidizing Substances in the Atmosphere of a Number of American Cities*, July 10, 1953, to July 10, 1954, a final report prepared by the Kettering Laboratory for the American Petroleum Inst., Sept. (1954).

(6) F. E. Littman and R. W. Benoliel, "Continuous Oxidant Recorder," *Anal. Chem.* **25**, 1480 (1953).

(7) J. Cholak, L. J. Schafer, W. J. Younker, and D. W. Yeager, "Air Pollution in a Number of American Cities," American Medical Association's *Arch. Ind. Health* **11**, (1955). (In press.)

TABLE 1

The Concentrations of Sulfur Dioxide as Determined by Different Methods, Particularly When Oxidant Levels Were Low

City	A. Oxidant as Recorded (Parts Per Hundred Million)	B. Sulfur Dioxide by Alkaline-Iodine Method (Parts Per Hundred Million)	C. Sulfur Dioxide[a] from Sulfate (Parts Per Hundred Million)
Elizabeth,	0.4 (4.4)	20	32
N. J.	0.2 (4.5)	16	29
St. Louis, Mo.	0.8 (3.4)	17	25
	1.2 (2.5)	10	14
	1.2 (2.5)	10	14
Akron, Ohio	0.5 (4.5)	7	19
	1.2	3	<1
	0.4 (0.7)	11	12
Detroit, Mich.	2.8	3	<1
	1.7	1	<1
Whiting-Hammond, Ind.		24	43

[a] Samples collected at same time as those in column B. Alkaline trapping agent was used, and sulfate was determined turbidimetrically.

TABLE 2

Average and Range of Concentration of Oxidant and of Sulfur Dioxide (Total Sulfate) in the Atmosphere of Certain American Cities

City	Oxidant		Sulfur Dioxide	
	Average (Parts Per Hundred Million)	Range (Parts Per Hundred Million)	Average (Parts Per Million)	Range (Parts Per Million)
Charleston, W. Va.	4.9	1.2 to 11.8	0.11	<0.01 to 0.63
Ann Arbor, Mich.	4.7	2.7 to 7.4	<0.01+	<0.01 [a]
Washington, D. C.	3.9	0.3 to 7.8	0.09	<0.01 to 0.35
Whiting-Hammond, Ind.	3.7	0.0 to 10.0	0.17	0.01 to 1.22
Cincinnati, Ohio	3.3	0.2 to 8.0	0.07	<0.01 to 0.33
St. Louis, Mo.	2.7	0.2 to 8.0	0.10	<0.01 to 0.43
Detroit, Mich.	2.6	0.8 to 5.5	0.02	<0.01 to 0.10
Philadelphia, Pa.	1.5	0.0 to 5.0	0.09	<0.01 to 0.22
Akron, Ohio	1.1	0.2 to 3.2	0.09	<0.01 to 0.22
Elizabeth, N. J.	0.9	0.0 to 2.8	0.20	<0.01 to 0.38

[a] Recorded by Thomas Autometer.

centration of sulfur dioxide indicated in these charts represent the averages for the several periods of sampling and do not portray the peaks which may have occurred during the period.

If the interference by nitrogen dioxide is neglected, and if the extent of the oxidation of sulfur dioxide to sulfuric acid can be determined, then it appears that the maximum concentration of oxidant can be approximated by calculation. The absolute concentration of sulfur dioxide may be estimated from the result of the determination of total sulfate, and the extent of the oxidation of sulfur dioxide to sulfate is given by the difference between this value (column C) and the iodometric value listed under column B of Table 1. One-third of this difference then may account for the ozone which has been lost. Some of the calculated maximum levels of concentration are given in the parentheses of Table 1, which has been taken in part from another paper[7].

Review of Initial Investigation

In the initial investigation, 9 cities were chosen according to certain characteristics which are classified below: Each city was visited for a period of 7 to 10 days within the overall period extending from October 13, 1953, through June 22, 1954, the recorder being operated in each only during the hours of daylight. Samples for the determination of sulfur dioxide by the 2 methods referred to in Table 1 were also obtained during periods of 1 hr. each on 6 or 7 occasions each day. Table 2 summarizes the data relevant to oxidant and sulfur dioxide for each city. Table 3 gives the concentrations of oxidant found while samples were being collected for analysis for sulfur dioxide. The calculated maximum concentrations of oxidant, when the concentrations of Table 3 were corrected for the interference of sulfur dioxide as described hereinbefore, are listed in Table 4. The cities are arranged in Tables 3 and 4 in descending order according to their average levels of concentration.

Class	Characteristic	City
1	Heavy automobile traffic —minimum industry	Washington, D. C.
2	Oil refining plus general industry	Whiting-Hammond, Ind. Philadelphia, Pa. Elizabeth, N. J.
3	General industry, but minimum oil refining	Cincinnati, Ohio St. Louis, Mo. Detroit, Mich. Akron, Ohio
4	Heavy chemical industry —no coal burning except by industry	Charleston, W. Va.

The recorded levels of concentration of oxidant in all of the cities varied inversely with the levels of sulfur dioxide and were, in general, so low that the tracings did not provide any evidence of response to the fluctuations in solar radiation or motor traffic. However, in Charleston, W. Va., during 3 days of heavy, low-lying fog, the level of concentration of oxidant never fell to zero, although the peaks and troughs in the tracings appeared to be related to the concentrations of sulfur dioxide which were found to be present. Fig 3 shows a tracing made on a day when the highest levels of oxidant found during the entire survey were recorded. This placed Charleston at the top of the list in Table 3 and suggested that the intensity of the atmospheric pollution might, of itself, be a factor in the production of ozone. Philadelphia, Detroit, Akron, and Elizabeth are at the bottom of the lists in Tables 3 and 4. The weather in Elizabeth varied equally between clear and cloudy, but the low values of oxidant are attributed mainly to the high levels of sulfur dioxide. Very little clear weather was encountered in Akron, Detroit, and Philadelphia, and the low position of these cities, as listed in the Tables, may be attributed to the fact that photochemical conditions for producing ozone were not optimum during the periods when the tests were made. The calculated maximum concentrations of Table 4 are more suggestive of this possibility than are the oxidant values of Table 3.

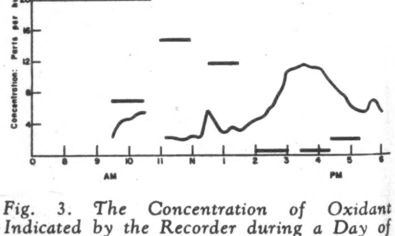

Fig. 3. The Concentration of Oxidant Indicated by the Recorder during a Day of Heavy, Low-lying Fog in Charleston, W. Va.

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[7] See footnote 7, page 227.

TABLE 3

The Levels of Concentration of Oxidant in the Atmosphere of Certain American Cities, as shown by Recorder Tracings.

(Concentrations Average over Period of One Hour—Taken While Samples Were Being Collected for Determination of Sulfur Dioxide)

City	Number of Samples	Average Concentration (Parts Per Hundred Million)	Range of Concentration (Parts Per Hundred Million)					
			0.0 to 1.99	2.0 to 3.99	4.0 to 5.99	6.0 to 7.99	8.0 to 9.9	10 and More
Charleston, W. Va.	42	4.8	1	9	22	10	..	..
Washington, D. C.	32	3.9	3	15	10	4	..	..
Cincinnati, Ohio	24	3.5	..	17	6	1	..	..
Whiting-Hammond, Ind.	44	3.1	11	14	16	..	..	..
St. Louis, Mo.	40	2.6	11	26	2	..	..	..
Detroit, Mich.	38	2.5	15	17	4	..	..	..
Akron, Ohio	36	1.1	33	7	..	..	..	..
Philadelphia, Pa.	36	1.1	30	3	..	..	..	..
Elizabeth, N. J.	41	0.9	37	9	..	..	..	..

concentrations of oxidant in the range of 0.0 pphm. to 1.99 pphm. were often indicated by the recorder in most of the cities (see Table 3). However, except for a single incident in Whiting-Hammond, values for the maximum concentration were in this range only in Elizabeth, Detroit, Akron, and Philadelphia.

Results of Continuous Long-Term Investigation

The findings of the initial survey indicated that Washington, D. C.—with little industry, but with dense population and heavy motor traffic—was also high on the list of cities investigated, with respect to the concentration of oxidant in the atmosphere. Because this city is also free from petroleum refineries, it was selected for a more intensive study in order to learn whether motor traffic appeared to play a part in the production of oxidant. The observations extended over a period of 85 consecutive days from September 23 through December 15, 1954, within which time temperature inversions occur most commonly.

An office on the second floor of a building at the corner of New York Avenue and 14th St., N. W., was selected as the sampling site. Sulfur dioxide was determined in the manner described hereinbefore, and inasmuch as nitrogen dioxide had been shown to be capable of contributing to the level of oxidant recorded by the instrument employed for that purpose[7], this contaminant was also determined independently at appropriate times. This was done by means of obtaining "grab" samples from time to time, and especially in coincidence with the occurence of peaks in the recorded levels of oxidant. In addition, the concentration of carbon monoxide in the atmosphere at the sampling site was determined periodically, in conjunction with estimations of the density of traffic made by counting the motor vehicles which passed a fixed point within a given period of time.

The results of these observations confirmed those of the initial survey in that the recorded concentrations of oxidant varied inversely with the levels of sulfur dioxide found. The advent of colder weather, with its greater demand for the combustion of coal, brought in its train concentrations of sulfur dioxide in the atmosphere which were higher, in general, than those observed during the previous year, and the recorded concentrations of oxidant were lower. The averages of the recorded concentrations of oxidant over the period of investigation, together with the corresponding levels of sulfur dioxide (from total sulfate), are shown in Fig. 4.

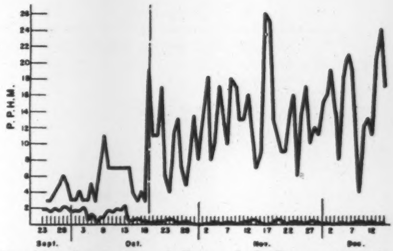

Fig. 4. Averages of Recorded Concentration of Oxidant, with the Corresponding Levels of Sulfur Dioxide, during 85 Consecutive Days in Washington, D. C.

The levels of concentration of sulfur dioxide in 498 samples collected at the rate of approximately 6/day during the test period are set down, according to the frequencies of their occurrence, in Table 5. The data in this and all subsequent tables are arranged according to 2 periods: the one is characterized by relatively warm weather; the other, by appreciably cooler weather. During the warm period from September 23 to October 18, only 7% of the average concentrations were in excess of 0.10 ppm.; in the colder period, from October 19 to December 15, 70% of the concentrations exceeded 0.10 ppm. The frequencies of the occurrence of the various levels of concentration of oxidant which were found while samples were being collected for the analysis for sulfur dioxide are compared for the warm and cold periods in Table 6. At no time during the period from September 23 to October 18 did the concentration of oxidant fall to zero. On the other hand, during the period from October 19 to December 15, the average concentration came within the range of 0.0 pphm. to 0.199 pphm. 149 times and, of these, 69 were zero concentrations. These low levels of concentration usually occurred

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[7] See footnote 7, page 227.

TABLE 4

The Corrected (a) Levels of Concentration of Oxidant in the Atmosphere of Certain American Cities

(Concentrations Average over Period of One Hour—Taken While Samples Were Being Collected for Determination of Sulfur Dioxide)

City	Number of Samples	Average Concentration (Parts Per Hundred Million)	Range of Concentration (Parts Per Hundred Million)					
			0.0 to 1.99	2.0 to 3.99	4.0 to 5.99	6.0 to 7.99	8.0 to 9.9	10 and More
Whiting-Hammond, Ind.	44	7.0	1	6	25	6	1	5
Charleston, W. Va.	42	6.8	..	3	21	10	5	3
Washington, D. C.	32	5.8	..	3	15	11	2	1
Cincinnati, Ohio	24	4.9	..	9	9	4	1	1
St. Louis, Mo.	40	3.9	..	22	16	2	..	..
Elizabeth, N. J.	41	3.3	20	11	4	4	1	2
Detroit, Mich.	38	2.6	15	17	6	..	..	..
Akron, Ohio	36	2.4	15	19	2	..	..	..
Philadelphia, Pa.	36	1.7	24	9	3	..	..	..

(a) See text for correction procedure.

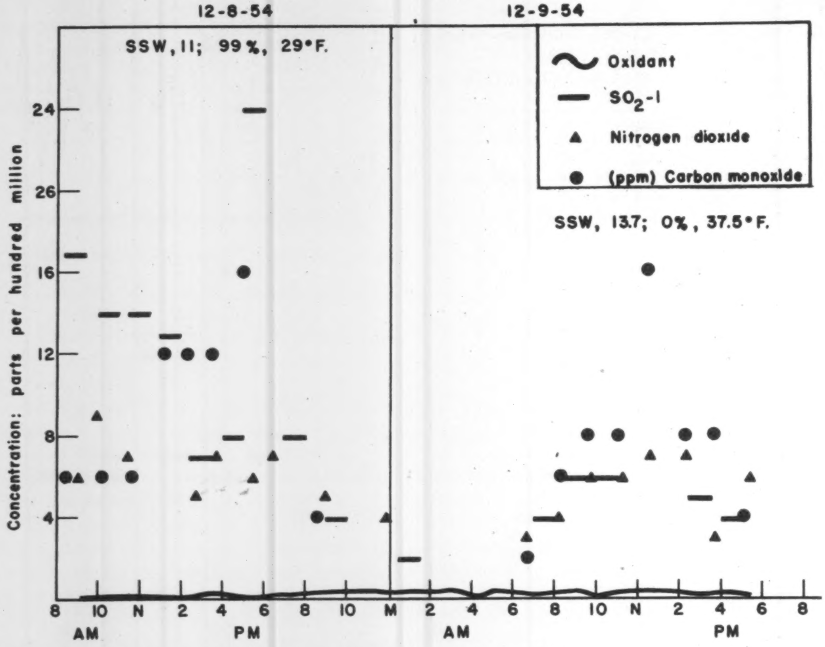

Fig. 5. The Concentration of Oxidant Indicated by the Recorder during 2 Successive Days of the Cold Period When the Actual Number of Hours of Sunshine Varied from 0 to 99% of the Maximum Number Possible.

during periods when the concentration of sulfur dioxide was high. The tracings recorded on 2 successive days during the colder period are reproduced in Fig. 5. December 8 was quite cold, but sunny, as is indicated by the value of 99%. This value represents the relationship of the actual number of hours of sunshine to the maximum number which might have characterized the specific day of the year, as indicated in local climatological bulletins issued monthly by the U. S. Weather Bureau. December 9 was a warm day, with no sunshine (0.0%) during the entire day. The records for these 2 days are shown because the oxidant recorder was operated through the night of December 8. On December 8 the recorder registered zero from 8.00 a.m. to 2.30 p.m., when relatively high concentrations of sulfur dioxide were present in the atmosphere. As the day wore on, the concentration of oxidant increased and then remained at a uniform level, near 0.4 pphm., during the night and most of the next day, December 9, 1954, when the concentration of sulfur dioxide was relatively low. No fluctuations resulting from variations in solar radiation could be detected in the tracings.

The levels of concentration of nitrogen dioxide and of carbon monoxide found during these 2 days are also shown in Fig 5. The concentration of nitrogen dioxide varied only slightly from the average value of 0.055 ppm. during the entire period. During these 2 days the concentration of carbon monoxide varied markedly and in apparent positive correlation with the density of motor traffic.

In an attempt to examine the relationship between the levels of oxidant in the atmosphere and the amount of solar radiation, the data in Table 6 were set against the proportion of sunny hours in the days involved. The data are so arranged in Table 7, in which the levels of concentration on days when the hours of sunshine exceeded 60% of the maximum are compared with those on days when such hours numbered less than 60% of the maximum. The data of the warm period suggest that the amount of sunshine is a factor in the production of oxidant, but those of the cold period fail to show a trend in this direction. This failure may well result from the effect of the relatively high levels of concentration of sulfur dioxide which, by their interference, reduced the oxidant to low levels.

Although these observations were so timed as to include the season when fogs were most likely to occur, it is of interest to note that only 5 of the 85 days were marked by sufficient fog to be so recorded in the local climatological bulletin. Four of these days occurred in succession, beginning on November 17, 1954. The tracings for the oxidant and the data for the other contaminants are

TABLE 5

Frequencies of Occurrence of Various Levels of Concentration of Sulfur Dioxide in Washington, D. C.
(Concentrations Average over Period of 1 Hr.)

Range of Concentration (Parts Per Million	Warm Period (September 23 to October 18)	Cold Period (October 19 to December 15)	Total (September 23 to December 15)
0.0 to 0.0249	32	12	44
0.025 to 0.049	39	29	68
0.05 to 0.0749	50	32	82
0.075 to 0.099	21	36	57
0.10 to 0.1249	9	72	81
0.125 to 0.149	1	34	35
0.15 to 0.1749	......	51	51
0.175 to 0.199	......	22	22
0.20 and more	1	70	71
Number of samples	153	358	511
Mean	0.054	0.136	0.112
Standard diviation	0.034	0.072	0.073

TABLE 6

Frequencies of Occurrence of Various Levels of Concentration of Oxidant in Washington, D. C.
(Concentrations Average over Period of 1 Hr.—Taken While Samples Were Being Collected for Determination of Sulfur Dioxide)

Range of Concentration (Parts Per Hundred Million)	Warm Period (September 23 to October 18)	Cold Period (October 19 to December 15)	Total (September 23 to December 15)
0.0 to 0.199	..	149	149
0.2 to 0.399	15	111	126
0.4 to 0.599	18	53	71
0.6 to 0.799	10	13	23
0.8 to 0.999	4	1	5
1.0 to 1.199	12	3	15
1.2 to 1.399	4	..	4
1.4 to 1.599	23	..	23
1.6 to 1.799	12	..	12
1.8 to 1.999	9	..	9
2.0 and more	30	..	30
Number of samples	137	330	467
Mean	1.300	0.265	0.569
Standard deviation	0.642	0.191	0.605

TABLE 7

Frequencies of Occurrence of Various Levels of Concentration of Oxidant in Washington, D. C., as Shown by Recorder

(Concentrations Average over Period of 1 Hr.—Arranged According to the Proportion of Sunny Hours in the Days Involved)

Range of Concentration (Parts Per Hundred Million)	Warm Period		Cold Period	
	Sunshine Greater than 60 %	Sunshine Less than 60 %	Sunshine Greater than 60 %	Sunshine Less than 60 %
0.0 to 0.199	..	..	59	90
0.2 to 0.399	4	11	36	75
0.4 to 0.599	11	7	28	25
0.6 to 0.799	6	4	9	4
0.8 to 0.999	2	2	..	1
1.0 to 1.199	5	7	..	3
1.2 to 1.399	4	..	..	..
1.4 to 1.599	17	6	..	..
1.6 to 1.799	12	..	..	..
1.8 to 1.999	5	4	..	..
2.0 and more	21	9	..	..
Number of samples	87	50	132	198
Mean	1.41	1.09	0.28	0.26
Standard deviation	0.59	0.68	0.19	0.19

TABLE 8

Frequencies of Occurence of the Maximum Concentration of Oxidant as Calculated (a)

(Concentrations Average over Period of One Hour)

Range of Concentration (Parts Per Hundred Million)	Warm Period (September 23 to October 18)	Cold Period (October 19 to December 15)	Total (September 23 to December 15)
0.0 to 0.99	25	38	63
1.0 to 1.99	21	52	73
2.0 to 2.99	51	85	136
3.0 to 3.99	29	79	108
4.0 to 4.99	9	32	41
5.0 to 5.99	..	17	17
6.0 to 6.99	..	11	11
7.0 to 7.99	2	6	8
8.0 and more	..	10	10
Number of samples	137	330	467
Mean	2.38	3.10	2.90
Standard deviation	1.26	1.89	1.74

(a) See text for method of calculation.

given in Fig. 6. The concentration of sulfur dioxide was relatively high on November 17 and 18, and the levels in the oxidant tracings were correspondingly low. The values for sulfur dioxide indicated by the solid line (SO_2—1) are absolute concentrations; those represented by the unbroken line (SO_2—2) were obtained by an iodometric method. The difference between the 2 values may be used to estimate the maximum concentration of oxidant (especially ozone) which could have been present at these times, provided any effect resulting from nitrogen dioxide is neglected. If the data of Table 6 are similarly reexamined so as to derive the maximum concentrations by calculation, the data of Table 8 result. The values are well within the range of 0.0 ppm. to 11 ppm. found by Cauer(8) in the atmosphere of certain European cities, and the range of concentration agrees with that found in Washington, D. C., in 1953. The concentrations found in 1954, as averaged hourly, are lower than those found in 1953, but this fact may result in part from the different locations of the 2 sampling sites—one in the downtown area; the other, a more open site at the edge of the downtown area.

The concentration of nitrogen dioxide remained at a substantially uniform level of approximately 0.05 ppm. during the entire 4-day period, but that of carbon monoxide varied widely from the average which is shown for each day, the peak (32 ppm.) occurring at 5:30 p.m. on November 19, 1954.

It is of interest to note that the general levels of the nitrogen dioxide in the atmosphere also varied in relation to the weather, whether warm or cold. This is illustrated by the data in Table 9, in which it may be seen that the concentration of nitrogen dioxide was generally higher during the warmer of the 2 periods. The effect of mixtures of nitrogen dioxide and sulfur dioxide on the concentration of oxidant, as portrayed by the tracing, is still uncertain, although the addition of nitrogen dioxide by itself will augment the height of the tracing yielded otherwise by ozone alone(7). The effect of the mixture is now being examined in the laboratory, and preliminary results show that the response of the recorder varies with the several interactions of these materials. That the concentration of nitrogen dioxide in the atmosphere may be appreciable at times is indicated in Fig. 7, which gives the record for September 28, 1954, when the peak value of 0.39 ppm. was recorded, after which the level diminished steadily as the day wore on. This pattern was noted on but few days.

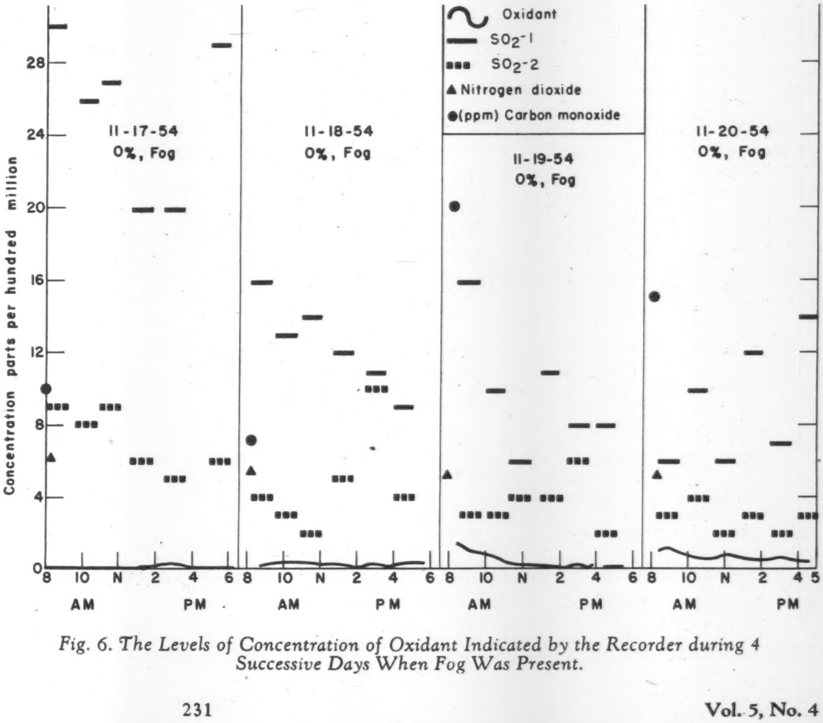

Fig. 6. The Levels of Concentration of Oxidant Indicated by the Recorder during 4 Successive Days When Fog Was Present.

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(8) H. Cauer, "Some Problems of Atmospheric Chemistry," *Compendium of Meteorology*, p. 1126, T. F. Malone, Boston, Mass., Boston American Meteorological Soc. (1951).

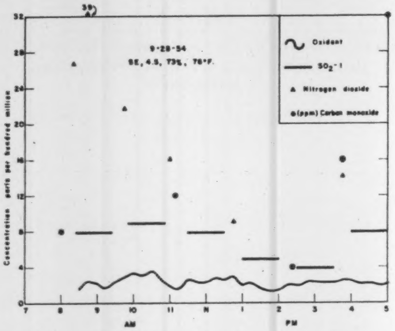

Fig. 7. The Concentration of Oxidant Indicated by the Recorder When the Concentration of Nitrogen Dioxide Was High.

TABLE 9

Frequencies of Occurrence of Various Levels of Concentration of Nitrogen Dioxide in the Atmospher e of Washington, D. C.

Range of Concentration (Parts Per Million)	Warm Period (September 23 to October 18)	Cold Period (October 19 to December 15)	Total (September 23 to December 15)
0.0 to 0.0249	2	64	66
0.025 to 0.049	8	197	205
0.050 to 0.0749	15	118	133
0.075 to 0.099	35	14	49
0.10 to 0.1249	17	4	21
0.125 to 0.149	8	. .	8
0.150 to 0.1749	5	. .	5
0.175 to 0.199	. .	. .	. .
0.20 and more	3	. .	3
Number of samples	93	397	490
Mean	0.094	0.043	0.053
Standard deviation	0.039	0.020	0.032

The concentrations of carbon monoxide which were found are given in Table 10 and, as in the case of oxidant and nitrogen dioxide, the concentrations were lower during the colder of the 2 periods. The role of motor vehicle traffic in the fluctuations in the concentration of nitrogen dioxide and carbon monoxide was investigated by means of comparing the levels of concentration of each of these pollutants at different periods of the day with the density of the traffic during the same periods (see Fig. 8). On the weekdays, including Saturday, the density of the traffic at the sampling station in the heart of the business district was maintained at a high level during the entire day, the peak occuring usually between 4 p.m. and 6 p.m. The highest concentration of carbon monoxide also occurred during this period. The concentration of the oxides of nitrogen remained at an essentially uniform level, between 0.04 ppm. and 0.06 ppm., regardless of the time of day. Analyses carried through the night showed that the level of carbon monoxide dropped off and that of nitrogen dioxide changed but little.

Summary

The determination of oxidant in the atmosphere of 10 Eastern and Midwestern American cities by the method used in the Los Angeles area demonstrates that the concentration of oxidant, as so determined and recorded, varies inversely with the concentration of sulfur dioxide present in the atmosphere. The levels of concentration of oxidant were generally so low as not to lend themselves, through quantitatively adequate fluctuations, to correlation with meteorologic variables. The photochemical production of ozone which appears to have occurred in Los Angeles and vicinity could not be confirmed in this investigation. Confirmation of the occurrence of this phenomenon elsewhere, within the range of this investigation, will require extensive — and probably intensive—observations carried out during periods when little or no sulfur dioxide is present as a source of analytical interference. No levels of concentration of oxidant above those which have been recorded as normal in other investigations were observed, except in Charleston, W. Va., during a period of heavy fog. The relatively high levels of concentration of oxidant which have been found in the atmosphere in Los Angeles during periods of fog and inversion were not encountered in the cities

(continued on page 248)

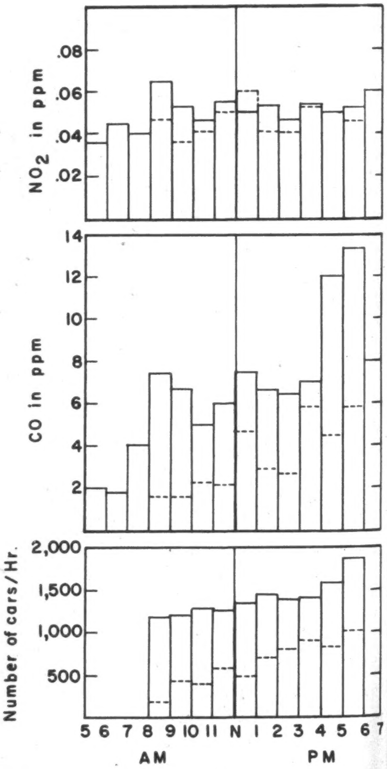

Fig. 8. Comparison of the Levels of Concentration of Carbon Monoxide and of Nitrogen Dioxide with Density of Traffic during Different Periods of the Day. Solid lines indicate weekdays, including Saturday; dashed lines indicate Sundays and holidays.

TABLE 10

Frequencies of Occurrence of Various Levels of Concentration of Carbon Monoxide in the Atmosphere of Washington, D. C.

Range of Concentration (Parts Per Million)	Warm Period (September 23 to October 18)	Cold Period (October 19 to December 15)	Total (September 23 to December 15)
0.0 to 1.99	7	62	69
2.0 to 3.99	15	88	103
4.0 to 5.99	17	113	130
6.0 to 7.99	7	18	25
8.0 to 9.99	28	56	84
10.0 to 11.99	. .	1	1
12.0 to 13.99	14	21	35
14.0 to 15.99	. .	. .	. .
16.0 to 17.99	17	22	39
18.0 to 19.99	. .	. .	. .
20 and more	3	5	8
Number of samples	108	386	494
Mean	9.00	5.92	6.59
Standard deviation	5.30	4.50	5.05

Air Soiling Potential—Automatic Filter Sampling

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This report furnishes some data on the particulate loading of air in a West Coast community and compares it with similar data from another part of the country. The data are from one year's observations of the soiling potential of air at a single outdoor station on the Berkeley campus of the University of California and were obtained by repeated 2 hr. samplings on filter paper with the A.I.S.I. automatic smoke sampler described by Hemeon *et al.*(1,2). The 12 sampling periods/day were nearly continuous, with occasional lapses, so that the equivalent of about 40 days of scattered observations were missed between May 1, 1954 and April 30, 1955.

The automatic sampler removes suspended particles from a known volume of air by filtration, mechanically positioning a fresh surface of Whatman #4 filter paper at regular intervals. For this study, filter paper soiling was measured by a light transmission technique, illustrated in Fig. 1, similar to that described by Hemeon. A Photovolt illuminometer with a special housing for the sensing element served as the transmissometer.

The sampling station was located on the roof of a 3 story building about 370 ft. above sea level, near a street but several hundred yards away from any evident source of smoke. For protection from the weather the sampler was placed in a box open only on the east side.

The waterfront industrial section of the city, as shown in Fig. 2, is about 3,500 yd. west of the sampling station, that is, essentially to windward during much of the year. The major commercial section is nearly 1,000 yd. west, otherwise the immediate vicinity of the sampling site is campus and residential in character. Fuels used in the area are almost exclusively gaseous and liquid, with natural gas strongly predominating for domestic use and used in half or more of the industrial and commercial establishments(3). Larger industrial communities with similar fuel characteristics are situated south of Berkeley and west across San Francisco Bay.

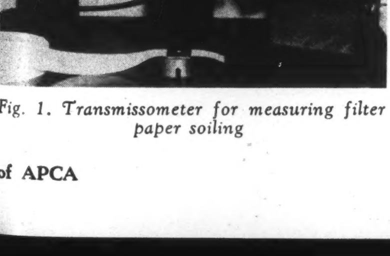

Fig. 1. Transmissometer for measuring filter paper soiling

Monthly averages of filter soiling in Berkeley, in COH units/1,000 ft.(2), are shown in Table I. The range of similar figures reported by Hemeon for a 15 mo. period(4) is given in the last line of the table to provide a comparison with data from a residential section of Pittsburgh, Pennsylvania.

Monthly average readings in Berkeley, as well as maxima and minima for 2 hr. and 24 hr. periods were well below the ranges reported by Hemeon(4). In every month, filter samples from many 2 hr. periods were totally free of observable soiling, in fact, some daily periods were so clean that is was difficult to find the exposed spots on the filter strip. On the other hand, when "smog" or "smaze" was considered present in the area, a decided increase in the soiling characteristics of the air at the sampling point was observed.

Yearly averages of 2 hr. observations for different days of the week are presented graphically in Fig. 3. All observations for a given period of the day are averaged for the 5 weekdays collectively and for Saturdays and Sundays separately. As shown in the graph, week days averaged more soiling than either Saturdays or Sundays, with the Sunday average about 60% of the week day average.

The yearly averages of 2-hr. observations for each day of the week separately are shown in Fig. 4. A continuous line connects the points for an average week, and the dashed line shows the trend of daily minimum soiling. It is obvious that a mid-day peak in soiling occurred on all days of the week, with a diminution in soiling potential after noon. It is also evident that as the average week progressed from the point of lowest smokiness on Monday morning to that of Friday morning, the increase in daily minimum soiling power was just barely perceptible, while the decrease in the early morning minimum from Friday to Sunday was quite evident. By far the least soiling occurred on Sundays.

Discussion

Although these data were collected from a single sampling station, we have observed that on days when obvious soiling of filter paper samples occurred on campus, a general haze was noticeable over a wide area of the community. In other words, our subjective observation

TABLE I

Monthly Average Soiling Characteristics of Air in Berkeley—COH/1,000 Ft.

Month	Monthly Average(a)	For 2-Hr. Period		Averages for 24-Hr. Period	
		Max.	Min.	Max.	Min.
May, 1954	0.7 (371)	2.5	0.0	1.1	0.2
June	0.6 (359)	2.8	0.0	1.1	0.1
July	0.7 (372)	4.0	0.0	1.7	0.1
August	0.5 (210)	2.8	0.0	1.3	0.2
September	0.6 (360)	2.8	0.0	1.0	0.3
October	0.7 (326)	3.5	0.0	1.4	0.3
November	1.0 (330)	4.0	0.0	2.4	0.1
December	1.2 (341)	4.0	0.0	2.5	0.2
January, 1955	1.3 (225)	4.0	0.0	2.6	0.0
February	0.7 (336)	2.8	0.0	1.7	0.1
March	0.5 (364)	3.5	0.0	1.1	0.1
April	0.3 (347)	3.3	0.0	0.9	0.1
Pittsburgh, Pennsylvania	6.5-2.2	11.3-6.6	1.8-0.2	10.1-3.1	2.2-0.9

(a) Figures in parenthesis are number of observations.

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(1) Hemeon, W.C.L., Sensenbaugh, J. D., and Haines, G. F. Jr., "Measurement of Air Pollution," *Instruments*, **26**, 566 (April 1953).

(2) Hemeon, W.C.L., Haines, G.F. Jr., and Ide, H. M., "Determination of Haze and Smoke Concentrations by Filter Paper Samplers", *Air Repair*, **3**, 22 (Aug. 1953).

(3) Proposed Air Pollution Criteria, City of Berkeley; Tebbens, B.D., Communication to City Manager, Jan. 1954.

(4) Hemeon, W.C.L., and Ide, H.M., Discussions of Paper "Automatic Filter Paper Sampler in an Air Pollution Measurement Program", *Air Repair*, **4**, 147 (Nov. 1954).

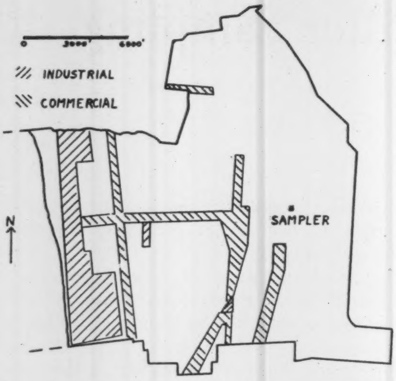

Fig. 2. City of Berkeley, showing principal industrial and commercial areas and sampling station

substantiates what was pointed out by Gruber⁽⁵⁾ and by Hemeon⁽⁴⁾, that smoke soiling measurements from a single sampling station may be representative of a rather extensive area. If this is the case (and there were no nearby smoke sources to upset the data), it indicates that a residential section of Berkeley, California, has, on the average, much cleaner air than a residential section of Pittsburgh, Pennsylvania

A comparison of results shown in Fig. 3 with those reported by Gruber and Alpaugh⁽⁵⁾ for 6 hr. periods at Cincinnati, Ohio, indicates that Berkeley is also relatively cleaner than Cincinnati. In both cities, week days averaged more soiling than Saturdays or Sundays, although the difference is much more pronounced in Berkeley than in Cincinnati. The average air soiling potential in Cincinnati on Sundays was about 80% of the weekday average, while in Berkeley the Sunday average was about 60% of the weekday. Although Gruber and Alpaugh used light reflectance rather than transmission for measuring the soiling characteristics of air, results of the 2 studies should be comparable since both used the same sampling method.

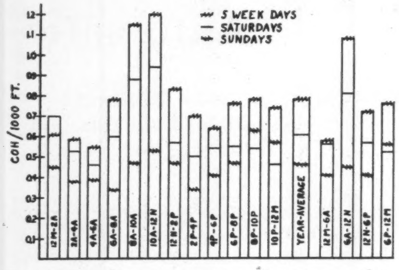

Fig. 3. Graphic presentation of average soiling characteristics of air for the year May 1954-April 1955. Average data by 2-hr. sampling periods for weekdays, Saturdays and Sundays.

In considering the diurnal pattern of smokiness illustrated in Fig. 4, it is difficult to distinguish the effects of air pollution sources from meteorologic variables, as similarly noted by both Gruber⁽⁵⁾ and Hemeon⁽⁴⁾. It is observed that the build-up in soiling power to a midday peak coincides with the increasing activity in community life beginning in the early morning hours. However, it is probable that the decrease in soiling potential after mid-day results from the frequent development of a westerly wind and the dispersal of inversion conditions, rather than from any abrupt change in community activity.

There seemed to be no appreciable accumulation of particulate smoke pollution during the average work-day week, as evidenced by the daily morning minimum, although the average decrease in soiling potential from Friday morning to Sunday morning was quite apparent. By implication, wind drainage and other pollution dispersing mechanisms are just capable, during the average week, of balancing the pollution load.

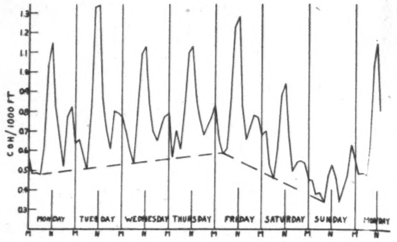

Fig. 4. Average soiling characteristics during 2-hr. sampling periods by day of the week

Since weather patterns are not affected by day of the week, the striking difference in Sunday smokiness as compared with that of other days seems primarily related to air pollution sources. A number of community activities are significantly diminished on Sundays, including commercial sales and services, industrial operations, and transport of persons to and from their place of work or other interests. While quantitative data is not readily obtainable on many community activities, some information is available concerning automotive transport at a location about 8,200 yd. southwest of the air sampling point. Data were obtained from the California Department of Public Works, and represent the daily traffic load on the San Francisco-Oakland Bay Bridge, averaged by day of the week, for the year coinciding with the year of air sampling. Results are given in Table II.

TABLE II

DAILY AVERAGE VEHICULAR TRAFFIC —TRANSBAY BRIDGE

May 1, 1954—April 30, 1955

Day	Average Number Vehicles
Monday	87,335
Tuesday	86,480
Wednesday	87,677
Thursday	87,547
Friday	95,016
Saturday	80,128
Week-days—Monday	80,616
through Friday	88,811

It is clear that daily vehicular traffic at the bridge is somewhat greater on weekdays than on weekends. However, Sunday traffic is 91% of the weekday average, while the Sunday soiling power is only 59% of the weekday average. Because of the distance separating the points of observation, we cannot conclusively determine from this data the contribution of automotive transportation to air soiling power. It is indicated, however, that such transport is fairly constant overall in the community on every day of the week, and that other sources of pollution are significantly involved in air soiling.

The data presented here primarily for comparative purposes show that much more elaborate studies of the variations in community activities are required to elucidate the factors in air soiling potential, and particularly to clarify the causes of relatively slight air pollution on Sundays as compared with other days of the week. While collecting information discussed in this paper, we have been impressed with the A.I.S.I. smoke sampler as a simply-operated mechanism for obtaining an index of air pollution in a community. As Gruber and Alpaugh⁽⁵⁾ pointed out and Hemeon⁽⁴⁾ affirmed, the sampler should be a highly satisfactory instrument for correlating a more exhaustive study of air pollution sources than has been presented here.

⁽⁴⁾ See footnote 4, page 233.

⁽⁵⁾ Gruber, C.W. and Alpaugh, E.L., "The Automatic Filter Paper Sampler in an Air Pollution Measurement Program", *Air Repair*, 4, 143 (Nov. 1954).

Meteorological Factors Affecting Causes and Controls of Air Pollution*

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Air pollution may be defined in various ways. One simple classification would specify contaminants as *natural* or *artificial.*

The artificial contaminants are the ones to which most attention has so far been devoted by individuals and organizations which have been concerned with the problem of air pollution. Typical artificial contaminants are industrial gases, fumes, and particulates; exhausts from motor cars, buses, trucks, locomotives, and aircraft; products from incinerators, both private and public; and radioactive debris from atom and hydrogen bomb testing.

Natural contaminants are substances which would be in the atmosphere even without man's activities. Examples of natural air pollution are salt particles from the oceans; volcanic emissions; pollens, spores, rusts, and smuts; sand particles raised by the wind; forest and brush fire smoke; and bacteria and viruses. Although some of these may be beneficial, they may also be harmful in varying degrees.

It is difficult to draw a sharp dividing line between natural and artificial pollutants. At times natural air pollution may be increased artificially by human activities. Land use practices may permit soil erosion by the wind; they may also increase the numbers of airborne pollens, spores, rusts, and smuts. Human carelessness as well as lightning discharges may and do start forest fires.

Our knowledge of weather and climate should be put to the fullest possible use in controlling both artificial and natural pollution. The atmosphere is a natural resource which, used wisely, is capable of aiding substantially in the innocuous disposal of many industrial wastes.

Dispersion by the Atmosphere

The word "dispersion" is used here to denote the scattering of gases and particles in the atmosphere, so that they leave their source and become progressively less concentrated. There are a number of atmospheric processes which lead to dispersion of contaminants.

Transport by Winds

The wind direction at a given time determines the general area into which a mass of gas or a cloud of particles will move. The wind speed closely specifies how rapidly the contaminant will advance into that area. Other things being equal, the concentration at a point downwind from the source will be inversely proportional to the wind speed.

In rough terrain it cannot be assumed that the wind direction and speed near the source govern the subsequent motion of the contaminant. Hills may deflect the air flow either horizontally or vertically or both, the amount of deflection depending on the vertical stability of the atmosphere. In valleys the wind carrying a pollutant tends to flow either up or down valley, following its meanderings. The deeper the valley the more pronounced this channeling effect is.

Turbulent Diffusion

Molecular diffusion of contaminants in the atmosphere is entirely negligible. The mixing caused by the natural turbulence of the wind flow is the only significant agency in atmospheric diffusion. When the wind is very turbulent, diffusion is rapid: in such conditions the plume of smoke from a stack diffuses so rapidly that it can no longer be seen a short distance downwind. On the other hand, when the wind turbulence is much less, diffusion is slow and the plume may be seen extending for many miles.

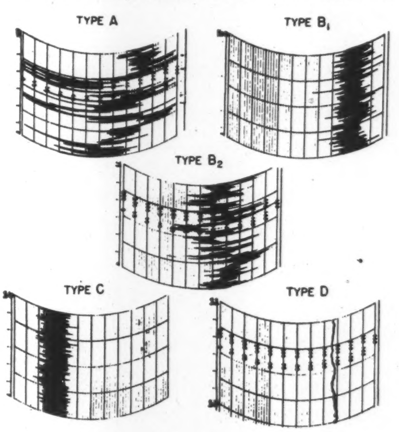

Fig. 1. Gustiness classification based on the traces made by a recording wind vane (after I. A. Singer and M. E. Smith).

The fluctuations of wind speed and direction may be used as indicators of turbulence and may be classified in various ways. The system developed by Hewson and Gill(1) relates diffusion conditions to ranges of gust accelerations as measured by a special instrument developed for the purpose. This procedure has the advantage of specifying diffusion in terms of a numerical quantity, the mean gust acceleration. The classification given by Singer and Smith(2) designates turbulence and diffusion according to the types of pen trace made by a recording wind vane. Their categories are shown in Fig. 1. Type A is the wind direction trace characteristic of thermal turbulence associated with extreme vertical instability in which diffusion is relatively rapid. Type C portrays mechanical turbulence is relatively rapid. Type C portrays mechanical turbulence induced by the rough underlying surface of the earth which also promotes rapid diffusion. Types B_1 and B_2 are intermediate, and represent combinations of thermal and mechanical turbulence. Type D shows the slight turbulence associated with marked vertical stability in an inversion layer, in which the temperature of the air increases upward. Vertical diffusion is at a minimum in such inversion layers.

Several theoretical analyses of diffusion from specified sources have been presented by Bosanquet and Pearson(3),

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*Presented to a meeting of the Industrial Research Institute, Houston, Texas, October 25, 1955.

(1) Hewson, E. W., and Gill, G. C., "Meteorological Investigations in Columbia River Valley Near Trail" in Report Submitted to the Trail Smelter Arbitral Tribunal. *U. S. Bureau of Mines Bull.*, No. 453, 23-228 (1944).

(2) Singer, I. A., and Smith, M. E., "Relation of Gustiness to other Meteorological Factors," *J. Meteor.*, **10**, 121-126 (1953).

(3) Bosanquet, C. H., and Pearson, J.L., "The Spread of Smoke and Gases from Chimneys," *Trans. Faraday Soc.*, **32**, 1245-1264 (1936).

(4) Sutton, O. G., "The Theoretical Distribution of Airborne Pollution from Factory Chimneys," *Quart. J. Roy. Meteor. Soc.*, **73**, 426-436 (1947).

(5) Frenkiel, F. N., "Application of the Statistical Theory of Turbulent Diffusion to Micrometeorology," *J. Meteor.*, **9**, 252-259 (1952).

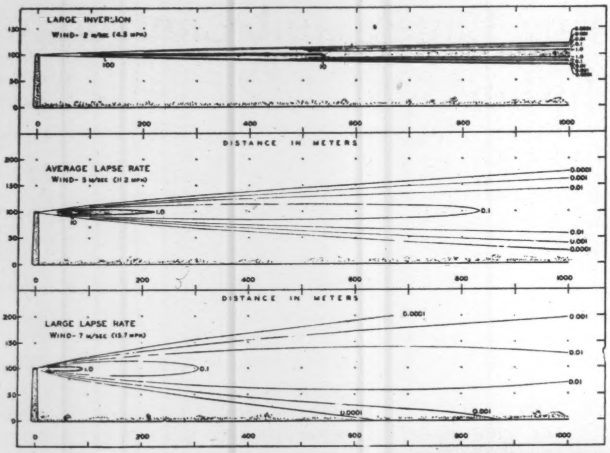

Fig. 2. The theoretical distribution of pollution from a 100-meter stack, based on Sutton's equations and values of the diffusion coefficients, the latter appropriate for a 3-min. sampling period. The concentration values, expressed in mg./meter³, are calculated for a rate of emission of the contaminant of 1 gm./sec.

Sutton⁽⁴⁾, and Frenkiel⁽⁵⁾. The equations developed involve diffusion coefficients whose values vary with meteorological conditions, including atmospheric stability. This stability or lack of it is of primary importance in diffusion studies. In the free air, where surface influences are negligible, unsaturated air is unstable when the lapse rate of temperature exceeds 5½° F./1000 ft. The lapse rate is defined as the rate of decrease of temperature with increasing height. Near the ground a greater lapse rate is required for instability. The values of the diffusion coefficients are such as to specify slow diffusion when the air is very stable, as in an inversion layer, and turbulence is at a minimum; with less stability or with instability, turbulence is pronounced and the use of the appropriate values of coefficients leads to the small concentrations characteristic of rapid diffusion.

Unless the wind speed is low, the mechanical turbulence induced in the wind flow over rough terrain promotes rapid diffusion. Over level terrain there is less mechanical turbulence and diffusion tends to be slower. The values of coefficients also depend on sampling period, as brought out by Smith and Singer⁽⁶⁾.

Computed concentrations downwind from a stack obtained by using Sutton's equations are shown in Fig. 2. Values for typical large inversions, average lapse rates, and large lapse rates and for typical associated wind speeds are given. The diagram brings out clearly the widely differing plume characteristics. A recent comprehensive discussion of atmospheric diffusion theories is available⁽⁷⁾.

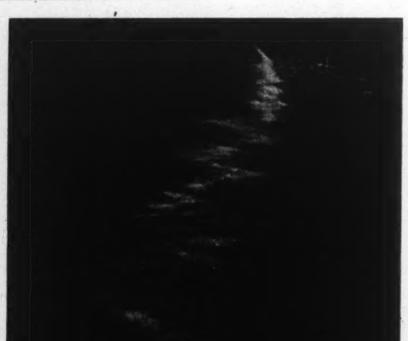

Fig. 3. The smoke plume from the 355-ft. experimental stack at Brookhaven National Laboratory in stable conditions. Vertical diffusion is very small, but horizontal diffusion is appreciable. Note the meandering of the plume, which shows the presence of large scale eddy motion in the horizontal.

The Inversion Breakup Process

Inversions may develop in a number of meteorological conditions. They often form at night just above the surface when the wind is low and the sky clear. The smoke plume will then extend downwind as a thin ribbon which gradually diffuses horizontally but diffuses vertically very little. Fig. 3 is a photograph of such an inversion plume from the 355-ft.-high experimental stack at Brookhaven National Laboratory, Upton, Long Island. The characteristic layering of the plume from the stacks of the Trail Smelter, in the Columbia River Valley, under similar conditions is brought out in Fig. 4.

After sunrise, solar heating causes a breakup of the inversion which brings the smoke to the ground in high concentrations by a process first described and explained by Hewson⁽⁸⁾. The process is portrayed in Fig. 5. Although ground concentrations are high, they persist for a limited period only, perhaps half an hour, and decrease exponentially thereafter. An approximate equation for mean breakup concentrations is available⁽⁹⁾.

Natural Cleansing of the Atmosphere

For the purpose of the present discussion, it will be assumed that natural cleansing occurs by one or more of the three processes: fallout, rainout, and washout.

Fallout

When the particles in a smoke plume are very small their vertical motion due to gravitational setting is negligible in comparison with that due to turbulence. It is probable that a good deal of removal of such fine particles is by a process of impaction on natural surfaces. The particles are whirled out of the air by centrifugal action in very small eddies occurring near natural surfaces. A mathematical expression for the concentration of fine particulates downwind from a continuous point source has been given by Chamberlain⁽¹⁰⁾. Meetham ⁽¹¹⁾ shows

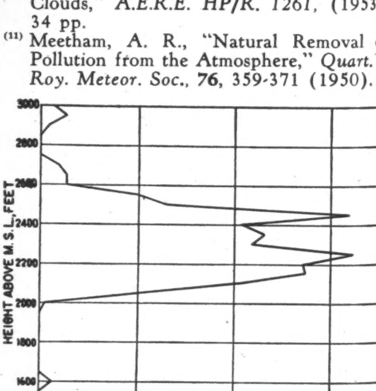

Fig. 4. Variation of SO_2 concentrations with height obtained by kite balloon measurements in the Columbia River Valley near Trail, B. C. Note the pronounced stratification under stable conditions (after E. W. Hewson and G. C. Gill).

(4,5) See page 235.

(6) Smith, M. E., and Singer, I. A., "Sampling Period in Air Pollution Evaluations," *Proc. Third Nat. Air Poll. Sym.*, Los Angeles, pp. 80-85 (1955).

(7) "Meteorology and Atomic Energy," U. S. Weather Bureau, Washington, pp. 38-58 (1955).

(8) Hewson, E. W., "The Meteorological Control of Atmospheric Pollution by Heavy Industry," *Quart. J. Roy. Meteor. Soc.*, 71, 266-282 (1945).

(9) Hewson, E. W., "Stack Heights Required to Minimize Ground Concentrations," *Trans. Amer. Soc. Mech. Engrs.*, *77*, 1163-1172 (1955).

(10) Chamberlain, A. C., "Aspects of Travel and Deposition of Aerosol and Vapour Clouds," *A.E.R.E. HP/R. 1261*, (1953), 34 pp.

(11) Meetham, A. R., "Natural Removal of Pollution from the Atmosphere," *Quart. J. Roy. Meteor. Soc.*, **76**, 359-371 (1950).

electron microphotographs of samples of smoke taken in the open air at Teddington, near London, in 1943. Two of the electron microphotographs are given in Fig. 6. From the various samples it was found that particles less than 0.075 μ in diam. constitute half the total number; only 10 particles in a million were larger than 2 μ in diam. Meetham calculates that it would take 46 days for a spherical particle of diameter 0.1 μ and density 2 to fall to the ground in still air from a height of 10 m.

For particles in the larger size ranges, gravitational settling is more important. The deposition of such particles on the ground has been analyzed by Bosanquet and Pearson(12), by Baron, Gerhard, and Johnstone(13), by Davies(14), and by Bosanquet, Carey, and Halton(15). A simple approximate procedure is to assume that the particles sink with a uniform speed, and to make allowance for this sinking by tilting the plume from a stack downward from the horizontal at a small angle specified by the ratio of the sinking speed to the mean wind speed(16).

Rainout

Rainout is the process by which contaminants contained in cloud particles are carried to the ground if and when the cloud particles grow to rain drops which reach the surface. Many small particles act as nuclei of condensation, and are thus removed in rain. Electron microscope studies of snow crystal growth in Japan in areas far from cities have been made by Kumai(17). He finds that a relatively large solid nucleus always exists at the center of a crystal, and that there are innumerable minute nuclei in the remainder of the crystal. Kumai refers to the former as the "center nucleus", and to the latter as "condensation nuclei". The center nucleus ranges in size from 0.5 to 8 μ; the diameters of the condensation nuclei vary from 0.01 to 1 μ. It is calculated that a dendritic plane crystal with a diameter of 1.6 mm. and a thickness of 10 μ contains about 10^7 of such nuclei with a diameter around 0.05 μ. Precipitation of such crystals, either as snow or after melting, as rain, may be an important way in which natural cleansing of very small smoke particles from the atmosphere occurs.

Since SO_2 readily oxidizes in the atmosphere to SO_3 in the presence of sunlight, and since SO_3 unites readily with water to form H_2SO_4, it would appear that an important mode of removal of SO_2 would be in rain.

Washout

When precipitation sweeps out contaminants during its descent, the process of removal may be termed washout. There is no doubt that some large smoke particles are collected and washed out by rain drops during their descent. Langmuir(18) deduces, however, that particles smaller than 1μ are not picked up by falling rain. Cleansing by this type of rain action is thus limited to removal of the larger particles. The rate of washout of the particles from a continuous point source has been analyzed by Chamberlain(19). Expressions for the rate of deposition by washout and for the maximum deposition arising from washout have been given(20).

Meteorology in Control Programs

There are many ways in which meteorological information and skills may be employed in the control of air pollution. The influences of both regional and local weather and climate should be considered. In one region the winds may be generally light and the diffusion of smoke and gases slow; in another the opposite may be true, with predominantly strong and variable winds and rapid diffusion. If a site for a new industrial plant is being considered, the pollution hazard will be minimized by choosing a geographical area of the country which has, in addition to other requirements, a climatic regime which is favorable for atmospheric diffusion. The important characteristics of a general region may be found by an analysis of a long term climatic record at a single representative station in the area or by an analysis of appropriate weather maps.

Once a suitable geographical area has been selected, then the micrometeorology —local features of weather and climate —of various possible plant sites should be examined. It is seldom realized how great the local variations in weather and climate may be. For example, there may be greater meteorological and climato-

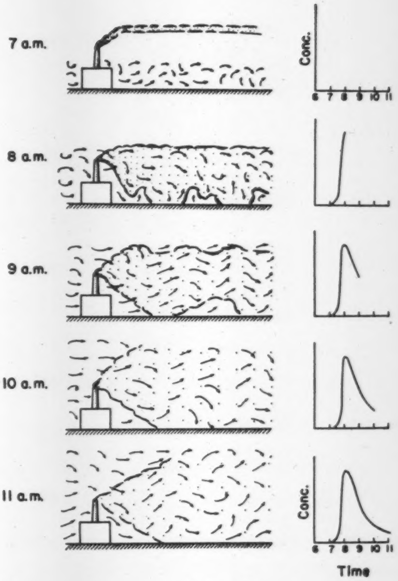

Fig. 5. The process of development of inversion breakup concentrations. As turbulence grows upward as a result of solar heating on a clear summer morning with light winds, gas is suddenly diffused downward from the plume aloft and produces high concentrations at the surface. The resulting variation of ground concentrations during the morning is sketched on the graphs at the right; note the sudden increase followed by an exponential decrease, which produces very high values for a period of about half an hour (after E. W. Hewson).

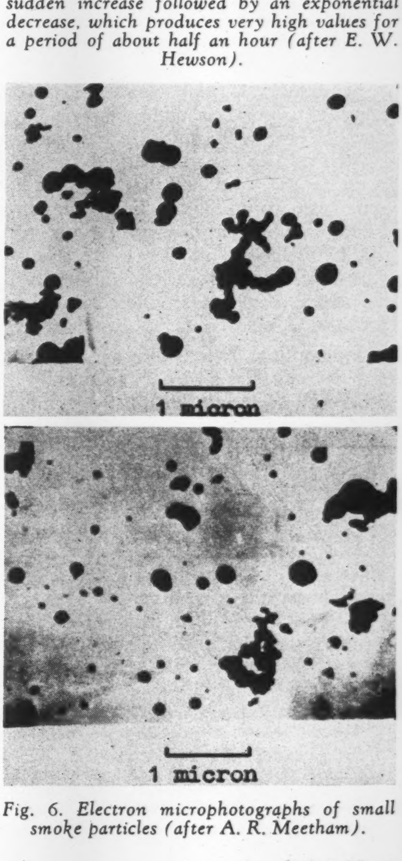

Fig. 6. Electron microphotographs of small smoke particles (after A. R. Meetham).

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(12) See footnote 3, page 233.

(13) Baron, T., Gerhard, E. R., and Johnstone, H. F., "Dissemination of Aerosol Particles Dispersed from Stacks," *Ind. Eng. Chem.*, **41**, 2403-2408 (1949).

(14) Davies, D. P., "The Lateral Diffusion of a Cloud of Falling Droplets," *Proc. Cambridge Phil. Soc.*, **46**, 500-507, Part III, (1950).

(15) Bosanquet, C. H., Carey, W. F., and Halton, E. M., "Dust Deposition from Chimney Stacks," *Proc. Instn. Mech. Engrs.*, **162**, 355 (1950).

(16) "Meteorology and Atomic Energy," U. S. Weather Bureau, p. 93 (1955).

(17) Kumai, M., "Electron-Microscope Study of Snow-Crystal Nuclei," *J. Meteor.*, **8**, 151-156 (1951).

(18) Langmuir, I., "The Production of Rain by a Chain Reaction in Cumulus Clouds at Temperatures above Freezing," *J. Meteor.*, **5**, 175-192 (1948).

(19) See footnote 10, page 236.

(20) "Meteorology and Atomic Energy," U. S. Weather Bureau pp. 96-98 (1955).

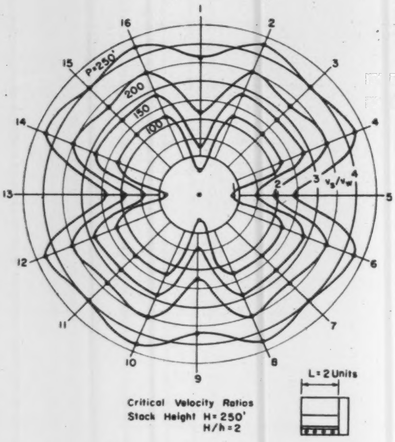

Fig. 8. Aerodynamic downwash occurring as the wind tunnel air flows diagonally across the model power plant (after R. H. Sherlock and E. J. Lesher).

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Fig. 7. Polar diagram giving critical ratios of stack gas exit velocity to wind velocity for a hypothetical model plant as a function of wind direction (after R. H. Sherlock and E. J. Lesher).

logical differences between various local areas in a city than there are between 2 cities several hundred miles apart. The local differences are dependent on topography; soil constitution; degree, type, and location of vegetation cover; location of built-up areas, etc., and are so complex as to require detailed meteorological measurements for their delineation. If such data are not already available, there is no alternative but to undertake a program of observations at one or more sites.

Even if the plant location has already been chosen, it is desirable to commence measurements of existing concentrations of contaminants and associated meteorological conditions before construction starts. These will provide a baseline for evaluating the contribution of the new plant to the local pollution after it has gone into production. Such measurements should continue during the construction period and for at least a full year after production starts in order to determine the actual pollution and its probable future limits.

Meteorology is in a position to contribute to control programs in a number of other specific ways. In addition to aiding in plant location, it may be helpful in plant design and in plant operation.

Shape and Orientation of Buildings

The work of Sherlock and Stalker(21,22) has shown that around some plants an aerodynamic downwash of stack gases occurs when the wind speed exceeds certain critical values. This critical speed varies with the aerodynamic properties of the building, with the direction of the wind, and with the stack gas exit velocity, and is conveniently evaluated by means of wind tunnel model studies.

The downwash is more pronounced when the wind approaches the building diagonally than for any other direction. A typical variation of downwash with wind direction is shown in Fig. 7, which is taken from the work of Sherlock and Lesher(23,24). For a building height of 125 ft. and a stack height of 250 ft., the curves give critical ratios of stack gas exit velocity to wind velocity required to maintain the base of the plume at heights of P = 100 ft., 150 ft., 200 ft. and 250 ft. To maintain the height of the base of the plume at 200 ft., the wind tunnel studies summarized in Fig. 7 show that for a southwest wind (direction 11), which is one approaching the plant building diagonally, the critical velocity ratio is 3.4, whereas for a wind parallel to the line of stacks of the plant, *i.e.*, from the west (direction 13), the critical velocity ratio is only 1.9. Fig. 8 is a photograph of pronounced downwash in the wind tunnel for a diagonal wind direction.

The shape of a building also influences downwash: large vertical walls increase its amount, and vice versa. A climatological study, such as that by Sherlock(25), of the frequency, duration, and directional distribution of strong winds will permit plant design and orientation so as to minimize this problem.

Stack Height

The pollution hazard is reduced by higher stacks. Costs also increase with stack height, and there may be other limitations on stacks, especially near airports. Stack costs in relation to height have been analyzed by Stankiewicz(26). A pressing problem in plant design is therefore the choice of a stack height which will minimize pollution and which will not be excessively expensive. The aerodynamic studies in wind tunnels by Sherlock and associates referred to above provide a convenient method of estimating the stack height and exit gas velocity required.

An analysis, using a synthesis of aerodynamic and meteorological considerations, for estimating stack heights required to minimize ground concentrations has been made by Hewson(27). Fig. 9 presents the end product of the study of the pollution hazard to be anticipated from a large midwestern power plant for

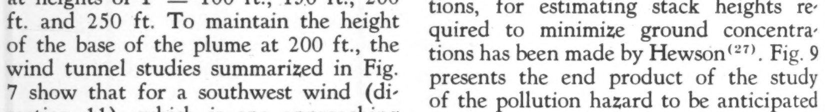

Fig. 9. Hours per year when the concentration of SO_2 in ppm. by volume lies within the limits indicated over the 22.5° segmental area to the northeast of the plant. SW wind; stack gas velocity = 120 fps. (after E. W. Hewson).

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(21) Sherlock, R. H., and Stalker, E. A., "The Control of Gases in the Wake of Smokestacks," *Mech. Eng.*, **62**, 455-458 (1940).

(22) Sherlock, R. H., and Stalker, E. A., "A Study of Flow Phenomena in the Wake of Smokestacks," *University of Michigan Engineering Research Bulletin*, No. 29 (1941) 49 pp.

(23) Sherlock, R. H., and Lesher, E. J., "Role of Chimney Design in Dispersion of Waste Gases," *J. Air Poll. Control Assoc.*, 4, 65-74 (1954).

(24) Sherlock, R. H., and Lesher, E. J., "Design of Chimneys to Control Down-Wash of Gases," *Trans. Amer. Soc. Mech. Engrs.*, *77*, 1-9 (1955).

(25) Sherlock, R. H., "Analyzing Winds for Frequency and Duration," *Meteor. Monogr.*, **1**, No. 4, 42-49 (1951).

(26) Stankiewicz, E.J., "How to Estimate Stack Costs," *Chem. Eng.*, June (1955) pp. 239-244.

(27) Hewson, E. W., "Stack Heights Required to Minimize Ground Concentrations," *Trans. Amer. Soc. Mech. Engrs.*, *77*, 1163-1172 (1955).

stack heights of 360 ft., 432 ft., 504 ft., and 576 ft. The wind is southwest and the stack gas exit velocity is 120 fps. The numbers in the boxes give the hours/year when the SO_2 concentrations will lie within the limits indicated at varying distances to the northeast of the plant. For example, with one stack 360 ft. in height there will be on the average 18 hr./yr. when the surface concentrations will lie between 0.5 and 1.0 ppm. in a 22.5° segment extending from 1.0 to 1.5 miles to the northeast of the plant. The 3 hr./yr. represent inversion breakup concentrations. With such information before him, the plant designer is in a position to choose a suitable stack height.

A primary problem in such an analysis is to determine the values of the diffusion coefficients to be used. Values appropriate for the 355 ft. experimental stack at Brookhaven, for the surrounding terrain, and for 1 hr. mean concentrations are given by Smith and Singer(28). When the source is near a ground surface of moderate roughness, the values mentioned by Mesler and Widdoes(29) may be used. It should be emphasized that many more field study programs should be undertaken in order to specify precisely the values appropriate for various meteorological and topographic conditions.

Varying Output of Contaminants

In certain industrial processes it is possible to vary the output of contaminants over a considerable range. Airborne wastes from plants with such flexibility may be disposed of advantageously by increasing emission when diffusion is good and reducing emission when diffusion is poor.

An example of such an operational procedure is the control regime for SO_2 adopted by the Trail Smelter in British Columbia(30). The upper limits of permissible sulfur emission depend on time of day, time of year, wind direction, and atmospheric turbulence, as shown in Table 1. The degree of turbulence is specified in terms of the bridled-cup gust accelerometer, as developed by Gill. Each change of wind speed of 2 mph. is recorded as a deflection in the trace made by a pen on a moving drum. The degree of turbulence is specified as the number of deflections/$^1/_2$hr.: this number is proportional to the mean horizontal gust acceleration, which is obtained in miles/hr. by multiplying the number of deflections by 4. Photographs of the gust accelerometer are shown in Fig. 14 and 15. The rate of diffusion is closely related to the gust acceleration, which is a prime characteristic of the turbulence field.

TABLE I

Maximum Permissible Sulfur Emission

(tons of contained sulfur per hour)

Time	Season	Turbulence(a)						
		0-74		75-149		150-349		>350
Midnight to 3 a.m.	Growing	2	6	6	9	9	11	11
	Nongrowing	2	8	6	11	9	11	11
3 a.m. to 3 hr. after sunrise	Growing	0	2	4	4	4	6	6
	Nongrowing	0	4	4	6	4	6	6
3 hr. after sunrise to 3 hr. before sunset	Growing	2	6	6	9	9	11	11
	Nongrowing	2	8	6	11	9	11	11
3 hr. before sunset to sunset	Growing	2	5	5	7	7	9	9
	Nongrowing	2	7	5	9	7	9	9
Sunset to midnight	Growing	3	7	6	9	9	11	11
	Nongrowing	3	9	6	11	9	11	11

(a) Deflections of gust accelerometer per half hour. Sulfur emission for unfavorable winds (left columns) and for favorable winds (right columns).

In some industries it may be possible to vary the output of contaminants with meteorological conditions without affecting production significantly. Where much coal is burned, as in coal-fired electrical generating plants, low sulfur coal may be burned during persistent periods of poor diffusion to reduce SO_2 output at such critical times.

Another possibility, which has not yet been explored adequately, is that of storing offending contaminants during periods of poor diffusion for release later to the atmosphere when diffusion is good. Although such storage may not be feasible now, the desirablility of designing new processes so as to permit storage for limited periods should be kept in mind.

The ideal solution to air pollution problems is to remove all contaminants at the source, provided that the materials so removed may be used advantageously in by-product manufacture. Unless they can be used in this way, the disposal or storage of the collected materials may become a serious problem. In the long run it may prove to be more economical to use the natural diffusing powers of the atmosphere when these are at their maximum for the disposal of wastes than it is to collect, haul to distant points, and dump them there. At times the diffusing capacity of turbulent winds is very large, and mixing so rapid that contaminants are dispersed into very small concentrations which cause neither annoyance nor damage. The atmosphere is a natural resource which can be both used and conserved by scientific management.

Special Operations

It may be necessary at times to dump fuming substances in the open air. Pollution problems can be avoided if such dumping is correlated with weather conditions in such a way that the fumes are carried away from inhabited areas and rapidly diffused. A forecast would specify not only diffusion and wind direction, but their persistence as well.

Emergency Precautions

In industrial operations there is often a danger that noxious gases or smoke will be accidentally — and suddenly — released. For example, there is always the possibility that an accident in an atomic power plant may lead to the release of radioactive materials. It is therefore necessary to have well-laid plans for the emergency evacuation of buildings likely to be affected. A survey of local weather and climate will show how far from the accident center the evacuation of personnel will be necessary.

Control of Pollution by Aeroallergens

There is 1 type of air pollution which affects 7,000,000 Americans, pollution by aeroallergens, the air-borne pollens, spores, rusts, and smuts which induce allergic reactions in sensitive individuals. Hay fever may appear to be a relatively innocuous malady, but, according to Sheldon *et al.*(31), the records show that 30 to 40% of individuals subject to hay fever will devolop asthma if the disease runs unchecked. The problem presented by aeroallergens merits more attention from air pollution control agencies than it has received in the past.

Ragweed presents the most serious problem in pollen allergy in the United States. It is widely distributed, as shown in Fig. 10. The annual deposition of ragweed pollen is very large in the triangular area whose corners lie in south-

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(28) See footnote 6, page 236.

(29) Mesler, R. B., and Widdoes, L. C., "Evaluating Reactor Hazards from Airborne Fission Products," *Nucleonics*, 12, 39-41 (1954).

(30) Dean, R. S., and Swain, R. E., "Report Submitted to the Trail Smelter Arbitral Tribunal," *U. S. Bureau of Mines Bull.*, No. 453, (1944) 304 pp.

(31) Sheldon, J. M., Lovell, R. G., and Mathews, K. P., "A Manual of Clinical Allergy," W. B. Saunders Co., Philadelphia, 1953, 413 pp.

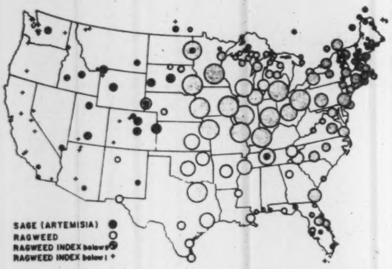

Fig. 10. Ragweed and sage (Artemisia) pollen counts for the continental U. S. and adjacent areas of Canada. Area of disc is proportional to total annual fall of pollen in each locality (after O. C. Durham).

eastern Texas, eastern North Dakota, and western Pennsylvania. It is more moderate in amount to the east of this triangle and nearly negligible to the west of it.

The distance that ragweed is transported by the wind has never been adequately studied. Discussions of the various meteorological and related factors involved in such transport have been given by Hewson[32] and by Dingle[33]. A comprehensive investigation of the whole problem of atmospheric pollution by aeroallergens is being undertaken at the University of Michigan under a research grant by the National Institutes of Health. An interdisciplinary team of research workers will explore the medical, meteorological, botanical, ecological, biochemical, and public health aspects of the problem. Fig. 11 shows preliminary measurements being made by automatic volumetric samplers of the horizontal distribution of the concentrations of ragweed pollen.

The possibility of taking effective steps to reduce the number of aeroallergens in the atmosphere in and around cities depends in part on how far they are transported by winds. The following statement by the British authority P. H. Gregory[34] is relevant:

> "It might be expected that once in the air, dry spores would mostly be carried far from their source, but under ordinary conditions this proves not to be so, and the bearing of this fact on plant pathology, fungus ecology, population genetics, and allergy is profound. Observations and theory agree that for spores or pollen liberated near the ground under normal conditions of turbulence, 99.9% of the spores will be deposited within 100 m. of the source. This is not to say that a very small proportion will not travel vast distances, but it is clear that most spores do not."

Fletcher and Velz[35] have pointed out that, if most pollen in the atmosphere travels only such short distances, pollinosis as an environmental public health problem in cities may be controlled by programs of spraying stands of ragweed in vacant lots and elsewhere with 2-4D or other suitable herbicides. Several programs of spraying have been initiated, but the benefits of the results have not been adequately assessed. The reduction of aeroallergen concentrations in city atmospheres to tolerable levels is a challenge to individuals and agencies concerned with air pollution.

Suggested Meteorological Programs

There is a strong need for many more field studies of pollution concentrations from specified sources in relation to meteorological variables. We require much more precise information on the variations of values of the diffusion coefficients with time of day, season of the year, topographic features, atmospheric stability, and height of source. A good deal of valuable information can be gained with a relatively unpretentious meteorological installation. A minimum program would include observations of wind speed and direction, atmospheric turbulence, and lapse rate taken simultaneously with concentration measurements at appropriate points. This minimum program applies only to the study of pollution from a single source, such as an industrial plant. The analysis of the pollution produced by a whole city must be handled in a different manner.

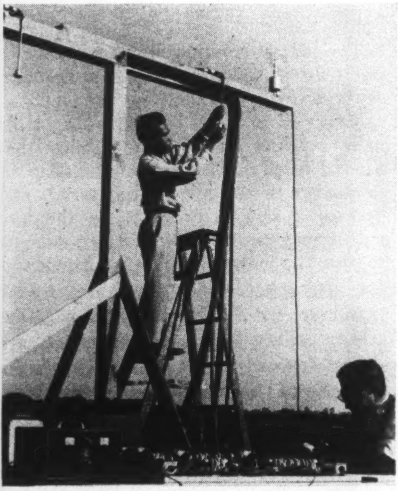

Fig. 11. Automatic volumetric sampling of ragweed pollen. Variations in the horizontal distribution are being measured.

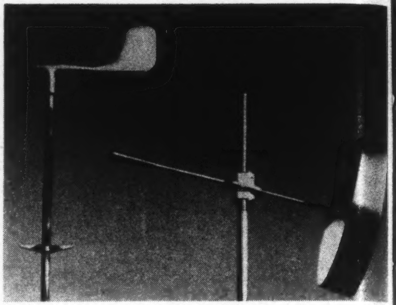

Fig. 12. The Bendix-Friez aerovane, l., and the all-weather bivane developed by D. A. Mazzarella at Brookhaven National Laboratory, r.

Wind Direction and Speed

A continuous record of wind direction is required in order to specify the area over which the contaminant has moved. An ordinary recording wind vane is adequate, or a combination wind vane and anemometer may be used. Such a combined instrument is the Bendix-Friez aerovane shown in the upper left hand corner of Fig. 12. Wind speeds are needed to ascertain the prevalance of aerodynamic downwash and for use in the concentration equations. Any one of a number of types of anemometers will be adequate, but the 3-cup anemometer and the aerovane are rugged instruments with good records of trouble free service. Suitable recorders for these instruments are readily obtained.

Atmospheric Turbulence

Turbulence may be measured in a number of ways. A special type of wind vane free to move vertically as well as horizontally, known as a bivane, is convenient for this purpose. The all-weather bivane developed by Mazzarella[36] at Brookhaven National Laboratory is shown in the lower right corner of Fig. 12. The bivane has the advantage of specifying both the vertical and horizontal components of turbulence, and hence of diffusion.

Two other types of bivane should be mentioned. The rapid response bivane

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[32] Hewson, E. W., "Atmospheric Pollution in Relation to Microclimatology and Micrometeorology: Some Problems," *Proc. Toronto Meteor. Conf.* 1953, Royal Meteorological Society, London, (1954) 240-252.

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[35] Fletcher, A. H., and Velz, C. J., "Pollens: Sampling and Control," in *Inservice Training Course in Air Pollution, February 6-8, 1950*, University of Michigan School of Public Health, Ann Arbor, (1950) 39-50.

[36] Mazzarella, D. A., "An All-Weather Remote-Recording Bivane," *Bull. Amer. Meteor. Soc.*, **33**, 60-66 (1952).

[37] Gill, G. C., in *Encyclopedia of Instrumentation*, University of Michigan School of Public Health, (in press).

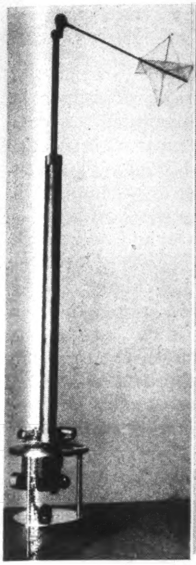

Fig. 13. Rapid-response bivane developed at M. I. T.'s Round Hill Field Station (after G. C. Gill).

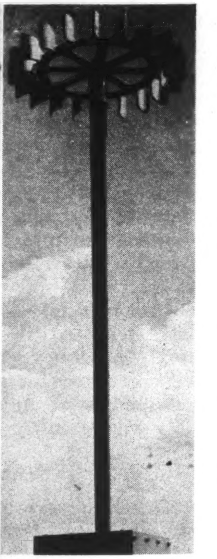

Fig. 14. Gust accelerometer for measuring atmospheric turbulence (after G. C. Gill).

developed by Gill(37) is shown in Fig 13; it features very low friction and inertia. Two microtorque potentiometers are used to specify the vertical and horizontal angular displacements of the vane. A counting bivane whose simplicity of operation recommends it for use in air pollution investigations has been described by Thomas(38) and by Thomas and Ivie(39). Ratchet and pawl mechanisms on both vertical and horizontal shafts of the bivane sum the total rotation in one direction of each shaft for any specified period of time. This total rotation is a measure of the turbulence.

The gust accelerometer mentioned earlier is also a convenient device for measuring turbulence(40). The horizontal wheel with vertical blades shown in Fig. 14 is bridled, so that the wheel rotates in one sense as the wind increases and in the opposite sense as it decreases. Each change in wind speed of 2 mph. causes an electrical pulse; the sum of the pulses during a given period may be recorded to give a number proportional to the mean horizontal gust acceleration during the period. Fig. 15 shows the interior mechanism. Both the counting bivane and the gust accelerometer have the merit of giving the turbulence directly as a number; there is therefore no problem of interpreting a rapidly fluctuating pen trace on a chart. The gust accelerometer has the additional advantage of being readily adapted to measure wind speed as well as turbulence, so that a separate anemometer is not needed.

The pressure-plate anemometer developed by Sherlock and Stout(41) and shown in Fig. 16 may also be used to measure turbulence. Plate A, housed in enclosure B, is kept normal to the wind by vane C. Deflection of the hinged plate A by wind pressure is resisted by spring D. Armature E is caused by the plate to move in the field of an electromagnet with coil F. The output from the system is recorded on a string oscillograph. This instrument responds well to small scale turbulence; its natural period of vibration is about 0.01 sec.

Lapse Rate Measurements

The rate of decrease of the temperature with height known as the lapse rate, is closely interrelated with turbulence and diffusion and hence is often measured. An inexpensive system of measurement is to suspend from a tower several recording thermometers, known as thermographs, in suitable shelters. The thermographs must be calibrated frequently if satisfactorily accurate lapse rate values are to be obtained.

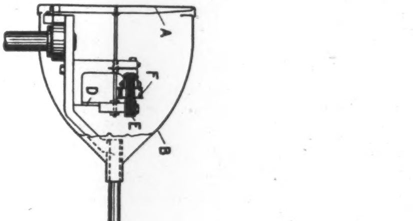

Fig. 16. Details of pressure-plate gust anemometer (after R. H. Sherlock and M. B. Stout).

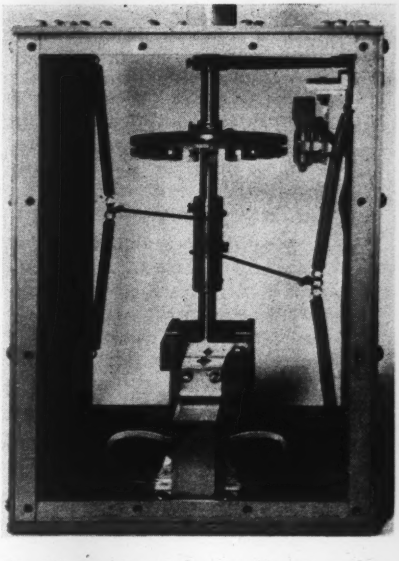

Fig. 15. Interior mechanism of gust accelerometer base (after G. C. Gill).

Instrument Mounting

A preferred exposure for the anemometer, wind vane, and turbulence instrument is several hundred feet above the ground and mounted on a tower. If a radio or television antenna tower is not available locally, light steel towers 100 ft. or more in height are available commercially at moderate prices. Thermographs should be spaced logarithmically along the tower, with closest spacing near the ground. With such a tower, the meteorological variables are measured in the air layers where the smoke plume moves and diffuses, not near the ground where surface influences predominate.

This suggested meteorological program is a minimum one, and is appropriate only for the analysis of pollution from a single source such as an industrial plant. Many worthwhile additions and refinements could be suggested for a more comprehensive meteorological analysis. A much more detailed description of a wide variety of meteorological instruments and techniques suitable for air pollution studies has been given by Hewson(42).

In closing, it should be emphasized that concentration measurements are an essential part of any program of meteorological studies in an air pollution survey.

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(38) Thomas, M. D., "The Present Status of the Development of Instrumentation for the Study of Air Pollution," *Proc. Second Nat. Air Poll. Sym.*, Los Angeles, (1952) 16-23.

(39) Thomas, M. D., and Ivie, J. O., "Wind Direction and Velocity Instrumentation for Air Pollution Diagnosis," *J. Air Poll. Control Assoc.*, 3, 41-44 (1953).

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Domestic Gas-Fired Incinerators

(continued from page 198)

a. Garbage requires from 2,000 to 8,900 Btu. of added heat/lb. for complete incineration. Normal amounts of paper and dry combustibles are not adequate for satisfactory incineration.

b. A good type A chimney is required for a domestic incinerator. This contributes to the retention of fly ash in the incinerator or dispersal of such particles as may escape at a reasonable height.

c. Screens, baffles, deflectors, and in some cases downdraft air contribute to more complete burning and reduction of smoke and odor.

d. Air for combustion is restricted, serving to control the rate of burning.

9. Severe restrictions are not necessary to prevent cities from being flooded with incinerators and possibly causing air pollution problem. Sales are not that easy to make. In 5 years' time our area has attained by strong promotional effort about 17% saturation.
10. The domestic incinerator industry is small, nationally. Like any other business, sales are necessary for the manufacturers to prosper, and to have money for further development and improvement. Restrictions would stop progress. Control of installations and encouragement of the manufacturers to improve their product should result in attaining the desired goal.

Incinerators of the Future

In 1952 a proposal was made to the American Gas Association that a research program on incinerator design and improvement be undertaken. This proposal was approved, a committee appointed to supervise the work, an outline of the project was prepared, and the work was assigned to the American Gas Association Laboratories in Cleveland and to Battelle Memorial Institute in Columbus, Ohio. The title of this project is "Elimination of Smoke and Odor and Potential High Temperature Hazards from Domestic Gas-Fired Incinerators." It is our objective to design prototype models which will produce essentially no smoke, no odor, no fly ash, and eliminate any potential fire hazard. Three methods of attack were proposed, namely, use of an after-burner, use of a catalyst, and smokeless combustion, as well as a study of methods for measurement of smoke and odor.

Research work was started in July, 1953, and has been continued at an accelerated rate ever since. It will continue through 1955 and into 1956 until the objective is reached.

Good progress has been made at both research institutions. The A.G.A. laboratories have designed and are in the process of assembling a prototype model using a gas-fired after-burner. All smoke and odor will pass through the flames or through a series of baffles heated by this burner and will be consumed. One of the experimental models used in this work for securing performance data and design information, as well as certain test equipment, is shown in Fig. 4. Battelle Memorial Institute, after considerable development work, is building a model employing a downdraft air principle of smokeless combustion, as well as a gas-fired after-burner. When both of these models have been tested to the satisfaction of the committee they will be demonstrated to manufacturers and interested utilities in the hope that similar models or modifications of them may be placed on the market.

Several manufacturers have also been doing considerable research and development along similar lines to the American Gas Association with the same general objectives. They have been encouraged by American Gas Association research, by interested utilities, by the comments of city officials, and the market potential for incinerators of this type. One manufacturer has already tested, to his satisfaction, and demonstrated to several groups, a new incinerator incorporating screens and catalyst heated by an afterburner which appears to accomplish the objective. During some tests with as foul a garbage mixture as would ever be discarded from a residence we observed no smoke or odor at the chimney outlet. Fly ash particles varied from 2 to 5 μ in diam. with invisible room air particles of 2 μ entering the unit. This new unit will be tested for approval at A.G.A. Laboratories at an early date and possibly will be on the market this summer.

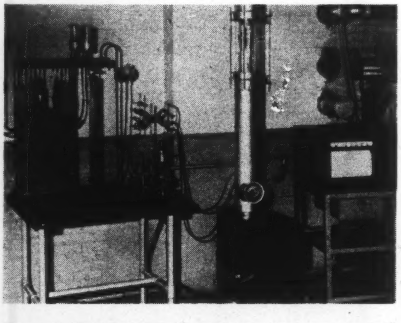

Fig. 4. Experimental incinerator constructed at A. G. A. Laboratories for developing an afterburner and baffle combination for consuming smoke and odor. White marks on side indicate grate location and 2 vertical baffles between which the smoke and flue gases pass downward through a gas flame and a hot baffle and upward to chimney. Gas analysis apparatus, a micrometer-operated slope gauge, temperature recorder, glass section in flue pipe, and automatic dust control are also shown.

Summary

This entire paper is a summary of the present status of domestic gas-fired incinerators and progress in research and development on them within the past 3 yr., but the major items presented are further condensed below:

1. Four factors have contributed to good incinerator installations in Cleveland. These include installation requirements, gas company test and inspection of new models, Cleveland permits required, and approval by a Cleveland City Board required.
2. Field experience has been good as measured by no smoke or odor complaints during a 4-wk. test period, very low service requests, a survey of installations and neighbors, opinions, and no complaints from a housing project with incinerators in each of 250 houses.
3. Ten reasons, with supporting facts, why contemporary domestic gas-fired incinerators should be acceptable to air pollution officials have been given.
4. American Gas Association research on incinerators, which has been in progress for nearly 2 yr. has as its objective providing design data and prototype model incinerators which will produce essentially no smoke, no odor, no fly ash, and safety from hazard of fire. This objective should be accomplished in 1955.
5. One manufacturer intends to market an incinerator with no smoke and no odor characteristics this year, possibly during the summer of 1955. Other manufacturers are making progress toward a similar objective.
6. A series of colored slides to be shown with this presentation will illustrate some of the progress being made on domestic gas-fired incinerators.

Survey of Gas-Fired Domestic Incinerators

(continued from page 202)

was used to determine the ignition temperature of the suet used in the test load.

It was found that the suet ignited and burned without applying open flame when the temperature reached 750 F.

When open flame was applied, the *flash point* was found to be about 550 F. The *fire point* was found to be about 650 F.

Flash point—Temperature at which a flash appears on surface when a test flame is applied under specified test conditions.

Fire point—Temperature at which ignition occurs and burning is maintained for 5 sec. under specified test conditions.

Based on the above findings and on the fact that stack temperatures from 970 F. and 1500 F. were observed during testing, the author concludes that the greases will add to the fire hazard.

Mold and Vermin

Based on the fact that it was virtually impossible to burn the simulated garbage load completely without agitation of the mass in the incinerator, the author concludes that there will always be a quantity of unburned garbage in the incinerator when in actual use, with the home owner as the operator. In addition, melted grease from average garbage can find its way into the ash drawer. The conditions in the ash pit and at points on the grate remote from the burner are almost ideal surroundings for the development of mold and vermin.

It was noted during the test of one incinerator that mold actually developed in the test load during the dehydration process preceding combustion.

Ash Disposal

Ash disposal may be a problem for the home owner who has no garden or rubbish can to put them in. The ashes cannot be dumped directly on the ground, since they are fine and powdery usually, and will blow all over the neighborhood unless carefully handled. Furthermore, the author believes that disposal of the ashes in gardens will soon become undesirable when done in the quantity produced by the incinerators over a period of time.

Hazard of Operation

The gas burner involved is no more hazardous to operate than other automatic gas appliances which have safety pilots, such as water heaters. However, a hazard involved in incineration definitely exists. This is:

> Sudden burning of a whole load after it has been dried out, resulting in a rush of flame from the incinerator into the area immediately occupied by the operator if the access door is opened. This hazard was noted a number of times during testing and the author concludes that it can happen at any time with any of the incinerators. However, it is believed to be more likely in the dehydrat-

(continued on page 244)

TABLE II

Results of Performance of Gas-Fired Incinerators

Incinerator	Combustion Type		Rated Capacity Bushels	Gas Rated/Input Btu./hr.	Test Duration Hours	Total Gas Cu. ft.	Smoke Gage Ref. No. (Garbage)	Agitations	Stack Temp. (Max.) Paper Run Deg.F	Weight Charge Lbs.	Energy Thous. Btu. Input	Input Btu./Lb. Charge	Residual Charge Lb.	Input Btu./Lb. Charge Burned
	Dehyd.	Rapid												
A		R	2	15,000	12.0	195	8+	1	1430	35	195	5570	0	5570
B		R	2	12,000	12.5	141.3	5	0	1300	35	141.3	4030	0	4030
C	D		2	2000 low 3000 high	93.5	326	8+	2	1350	35	326	9300	4.7	10,470
D		R	1.5	10,000	18.5	143	5	1	970	26.25	143	5450	0	5450
E		R	2	15,000	11.5	140.5	6	1	1180	35	140.5	4020	0	4020
F	D		2	2,000	64.5	130	8	0	1420	35	130	3720	0.75	3800
G	D		2	2,000	120	252	8+	3	1460	35	252	7200	2.75	7810
H		R	2	12,000	13.25	177.1	6	1	1170	35	177.1	5060	0	5060
I		R	2	12,000	10.5	159.5	8	3	1300	35	159.5	4550	0	4550
J	D		1	3,000	27.5	96.0	7	1	1180	17.5	96.0	5480	0	5480
K		R	2	12,000	13.8	165.5	8	2	1230	35	165.5	4730	0	4730
L		R	1	25,000	8.5	177.9	8+	1	1500	17.5	177.9	10,150	0	10,150
M		R	2.5	10,000	25.	225	7	1	1370	35	225	6440	14.5	11,000
N	D		1.5	1700 low 3000 high	52.	120	8+	2	1390	26.25	120	4750	2.0	4940

Reactions Involving Ozone, Nitrogen, Nitrogen Dioxide and Organic Compounds

(continued from page 225)

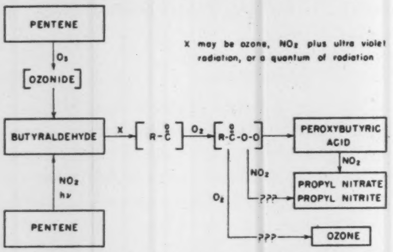

Fig. 13. Schematic Summary of Findings for 1-Pentene.

forms when ozone is mixed with aldehyde in nitrogen.

All straight-chain aldehydes from formaldehyde to heptaldehyde, inclusive, produce peroxy acid when reacted with ozone. Butyraldehyde produced the largest amount of the peroxy acid.

Peroxy acid is produced by the photochemical oxidation of aldehyde in air.

The dark reaction in nitrogen between peroxy butyric acid and nitrogen dioxide produces propyl nitrite. This suggests that the alkyl nitrite formed in the 1-pentene — nitrogen-dioxide and the 2-methylpentane-nitrogen-dioxide reactions actually is formed from peroxy acid.

Fig. 13 is a summary of the experimental findings on the reaction of the sample olefin, 1-pentene, with ozone or nitrogen dioxide in air under "sunlight" illumination. Saturated hydrocarbons presumably are converted to nitrite and nitrite in an analogous series of reactions.

The Future

All of the experiments described in this paper were made with partial pressures of reactants in the millimeter range. These are, of course, far higher than any which are ever encountered in any polluted outdoor atmosphere. To extend the studies to reactant concentrations more nearly representative of actual pollution conditions, a long-path infrared absorption cell has been constructed. This cell makes use of the multiple reflection system devised by White(11). With a base path length of 3 m. any integral multiple of 4 passes (12 m.) can be obtained up to the limits imposed by energy losses. With a path length of about 100 m. it should be possible to detect substances which are present at concentrations on the order of parts/million.

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(11) J. U. White, "Long Optical Paths of Large Aperture," *J. Opt. Soc. Amer.* 32, 285 (1942).

Survey of Gas-Fired Domestic Incinerators

(continued from page 243)

ing-type incinerator where drying takes place gradually and slowly.

Wall and Floor Temperatures

Temperatures measured on wall and floor surfaces were found to be within reasonable and safe limits except as noted in Table I.

Time of Operation

From the data obtained in the investigation, the author concludes that the rapid combustion type of incinerator tested will dispose of the garbage and rubbish produced by the average family in a reasonable time. However, the dehydrating type is very much slower and there is, in the data, evidence enough to indicate that the dehydrating type may not dispose of a relatively small charge of garbage in 24 hr. If the day's refuse cannot be disposed of that day, an undesirable condition results.

The author believes that it will not be feasible to design a domestic incinerator for use in metropolitan areas for the disposal of garbage. It may be possible to devise a combination system of disposal involving the domestic incinerator as a burner of a limited type of rubbish, and a garbage grinder for disposal of garbage with municipal collection for other types of combustible and non-combustible refuse. Since this will still involve collection, with need for maintaining a collection and disposal group with all of its problems, it seems to the author that possibly the land fill method is a logical solution in spite of its difficulties.

Recommendation

In view of the fact that:

(a) Although the use of the domestic incinerator would likely reduce the air pollution resulting from backyard burning, the pollution would still remain to an undesirable degree.

(b) Municipal collection problems will still remain, requiring the city to maintain a considerable department for collection and disposal of refuse which cannot be disposed of in the domestic incinerator.

(c) It is almost certain that air pollution will result from the use of the present type of domestic incinerator, particularly during garbage disposal.

(d) The home owner does not stand to benefit financially, since the original installation will cost from $100 to $200. Operating costs will be $2.00/mo. With the same expenditure/home, the city could be very well financed and in a position to do a better job of disposal than any group of home owner.

(e) City living involves problems which rural living does not, and these must be solved at some financial expense. If the expense is borne at home or in additional tax burden, the cost is still the same.

The author recommends that the use of gas-fired domestic incinerators should not be encouraged while municipal disposal methods are studied and developed, even at the need for additional taxes.

Acknowledgment

The author acknowledges the efforts of Mr. Oscar B. Noren, Instructor in Mechanical Engineering at the University of Detroit, who cooperated in the investigation described herein.

Much of the information set forth here is contained in the report of the tests completed in March, 1954.

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AIR POLLUTION CONTROL
COMBUSTION FUEL AND REFUSE BURNING
SMOKE CONTROL

Isokinetic Sampling

(continued from page 226)

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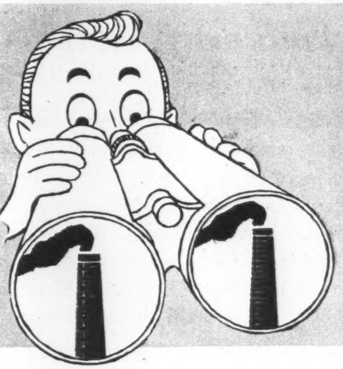


Look at Smoke through the Inspector's Eyes

Men who know most about the problem of air pollution agree that . . .

1 Everyone is anxious to avoid polluting the air because it means fuel waste as well as bad public relations.

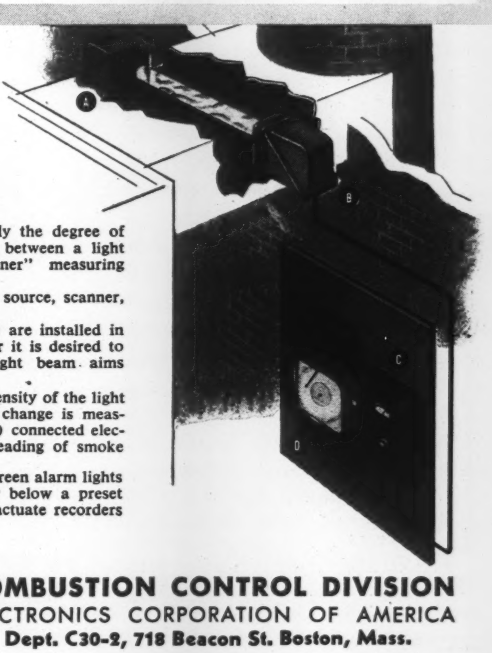
2 Most offenders have the false idea that good fuel burning equipment, properly installed will not pollute the air. Most owners tend to forget that any slip-up in operating or maintenance can mean smoke from the best equipment.

3 Too few offenders remember that operators or custodians are *inside* . . . that a man at the boiler front can't know *what* is coming out of the stack, or *when* smoke occurs. That means smoke and fuel waste are undetected . . . and failure to quickly correct the condition back of it.

4 What every fuel burner needs is a really effective smoke indicator and alarm to signal that something needs attention in order to stop the pollution and fuel waste.

A majority of pollution and fuel burning experts also agree that the most effective system for detecting smoke, and warning the operator, carries the name FIREYE. Below is a brief description. Send for the new Bulletin which tells all about FIREYE System FE-3. You'll find the cost is so low that even the smallest apartment house can have it. Meets all smoke ordinances. WRITE FOR BULLETIN, NOW.

HOW fireye SYSTEM FE-3 WORKS



Fireye System FE-3 measures directly the degree of obscurity of smoke or haze passing between a light source and a photoelectric "scanner" measuring element.

Three simple basic elements—light source, scanner, and indicator—comprise the system.

Light source (A) and scanner (B) are installed in a breeching, stack, or duct—wherever it is desired to measure smoke density—so that light beam aims directly at scanner lens.

As smoke density increases, the intensity of the light the scanner receives decreases. This change is measured by Smoke Density Indicator (C) connected electrically to scanner, giving a direct reading of smoke density.

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Formation of Ozone in Polluted Atmosphere

(continued from page 218)

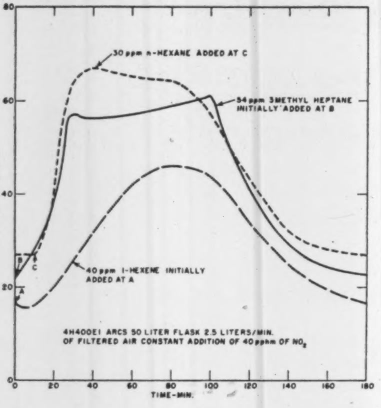

Fig. 9, Oxidant Formation in Irradiated Mixtures of Various Hydrocarbons with NO_2 in Filtered Air.

give a steady concentration of about 0.4 ppm. The air then flowed through an irradiated flask and then to an oxidant recorder. The recorder indicated any ozone formed by the photolysis of the nitrogen dioxide [equation (1)]

$$NO_2 + h\nu + O_2 \rightarrow NO + O_3 \qquad (1)$$

and measured a fraction of the nitrogen dioxide itself, usually about one-half. Upon the addition of an organic material to the air-nitrogen-dioxide mixture before the flask, an increase in the oxidant level took place if the organic material participated in or facilitated ozone formation. Usually the organic material was added all at once and the experiment was allowed to continue until the oxidant recorder showed a new steady state. Fig. 9 illustrates the technique with *n*hexane, 1-hexene, and 3-methyl heptane. Fig 10 demonstrates that the activated carbon filter was removing substances which lead to increased oxidant levels. Auto exhaust at 200 ppm., a concentration to be expected in smog, gave comparable results. Negative results were obtained with benzene and hexane, but positive results were obtained with most organics.

A Mechanism for Ozone Formation in Polluted Air

The observation that nitrogen dioxide is formed by the irradiation of polluted air and that nitrogen-dioxide organics form oxidant under concentration and light conditions comparable to smog is indirect evidence that such reactions are important to the formation of ozone in polluted atmospheres. That nitrogen dioxide is photolyzed to give oxygen atoms by light in the 3,000 Angstrom to 4,000 Angstrom region is well known[7,5]. That ozone is formed from oxygen atoms and molecules is also well known. The puzzling feature in understanding what happens in polluted air has been to get around the reverse reaction which limits the maximum amount of ozone which can be formed, as related by Cadle and Johnston[8]. Experiments on mixtures of nitrogen dioxide and pure air have tended to support their proposition [equation (2)] that a maximum concentration of 3 pphm. and 10 pphm. can be formed from 0.10 ppm. and 1.0 ppm. of nitrogen dioxide, respectively.

It has been proposed that the organics function in the air-nitrogen-dioxide-light systems,

$$\underset{\text{(this reaction is reversible)}}{NO_2 + h\nu + O_2 \rightarrow NO + O_3} \qquad (2),$$

by removing the nitric oxide which limits the ozone concentration. Such a hypothesis is compatible with the observation that irradiation of polluted air forms nitrogen dioxide rapidly. The known affinity of nitric oxide for free radicals makes it probable that a reaction of this type is involved. Equations (3), (4), and (5) have been suggested as possible reactions of this type.

$$NO + R\text{—} \rightarrow R\text{—}NO \qquad (3)$$
$$NO + R\text{—}O_2 \rightarrow NO_2 + R\text{—}O\text{—} \qquad (4)$$
$$NO + HO_2 \rightarrow NO_2 + HO \qquad (5)$$

Each of these equations is plausible and only experimentation can establish whether they are important under the conditions existing during smog.

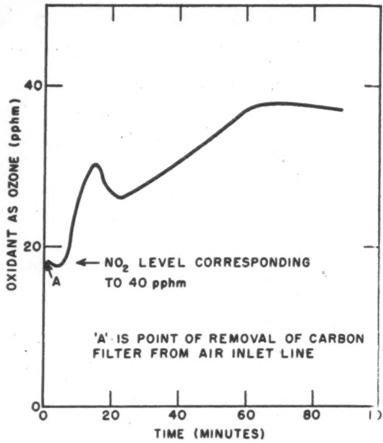

Fig. 10. Formation of Oxidant on Irradiation of Nitrogen Dioxide in Unfiltered Outside Air.

Summary

Nitrogen dioxide has been shown to be formed during the irradiation of polluted air when precursors are present, presumably from nitric oxide or organic nitrogen compounds. The photolysis of nitrogen dioxide in the presence of organics produces oxidants believed to be largely ozone. The organics probably assist the formation of ozone by reacting to give free radicals which remove the nitric oxide as an organic derivative or rapidly oxidize it back to nitrogen dioxide. Further experiments must be designed to permit a choice of the many possibilities.

Abbreviations and Symbols

---

m/e. . . .ratio of the mass of the fragment to the number of electrons lost during ionization.
h. . . . . . Plank's constant (6.55×10^{-27} erg-seconds).
v. . . . . . frequency of radiation.
pphm. . . parts per hundred million.

Acknowledgment

The experimental work on which this paper is based was largely carried out by Hadley Ford and Noboru Endow under the immediate direction of Fred Littman. Other members of the Department of Chemistry of Stanford Research Institute made substantial contributions which are collectively acknowledged.

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[5] See footnote 5, page 218.

[7] R. G. W. Norrish, "Photochemical Equilibrium in Nitrogen Peroxide—I," *J. Chem. Soc.* (London) 761-75 (1927). R. G. W. Norrish, "Photochemical Equilibrium in Nitrogen Peroxide—II: The Dependence of Quantum Efficiency on Wave Length," *J. Chem. Soc.* (London) 1158-69 (1929); R. G. W. Norrish, "Photochemical Equilibrium in Nitrogen Peroxide—III: A Comparison of the Thermal, Photochemical and Electrical Decompositions and a General Theory of the Change," *Ibid.* 1604-11.

[8] Richard D. Cadle and Harold S. Johnston, "Chemical Reactions in Los Angeles Smog," *Proc. 2nd Natl. Air Pollution Symposium, 28-34, Stanford Research Inst.*, May (1952).

Measurement of the Visibility of Air Pollution by Light Scattering

(continued from page 212)

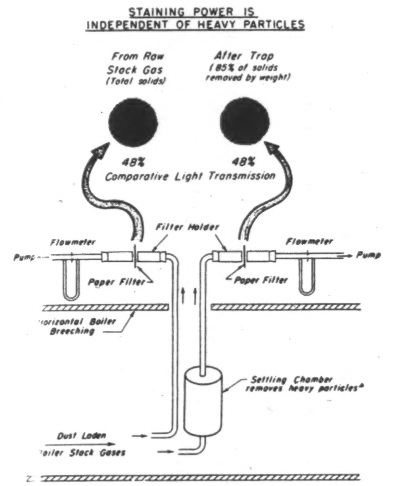
STAINING POWER IS INDEPENDENT OF HEAVY PARTICLES
From Raw Stack Gas (Total solids)
After Trap (85% of solids removed by weight)
48%
48%
Comparative Light Transmission
Filter Holder
Flowmeter
Flowmeter
Pump
Pump
Paper Filter
Paper Filter
Horizontal Boiler Breeching
Settling Chamber removes heavy particles
Dust Laden Boiler Stack Gases

Fig. 2. Demonstration of staining properties of dust laden stack gases

through which air samples have been passed. They have sampled dust-laden stack gases, and have shown that the removal of 85% by weight of solids had a negligible effect on the optical properties of the filter paper stain. Fig. 2, taken from the paper by Hemeon, Haines and Ide, illustrates this. In another experiment they sampled atmospheric air over a period of many days and demonstrated again that a filter which separated a major fraction of the weight of solids had very little effect on the stain produced. This is shown in Fig. 3. Sinclair(3) recommends that his light scattering instrument be calibrated by collecting the smoke on a filter and then weighing. This procedure seems questionable to the author. For this reason an instrument using air as a standard has been developed. Thus, it would be possible to relate the scattering properties of smoke to the scattering of pure air. Sinclair's method measures the scattering of air, but calibrates by means of weighing.

The measurements using air as a standard is unusual because the standard may be tens of hundreds of times smaller than the aerosol being measured. However, careful electronic and optical design has overcome this difficulty. Measurements obtained with different instruments of this type should be very comparable. Each instrument makes a ratio measurement. The scattering of a given volume of aerosols is compared to the scattering of the identical volume of air. A dimensionless ratio is obtained which cancels out numerous instrumental errors.

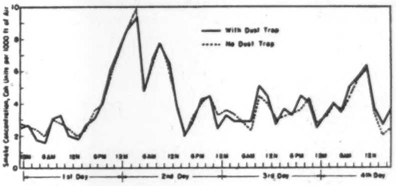

Fig. 3. Comparison of filterpaper smoke concentrations by 2 I.S.I. smoke samplers in parallel, 1 in stream passing through a marble dust trap

An example of a laboratory application of the instrument is given in Fig. 4. The instrument was tested in the 118,000 ft.^{3} auditorium of Mellon Institute. This figure shows what happens to the light scattering properties of the auditorium air when 2 cigarettes are smoked in succession. The five-hour experiment was made in the tightly closed auditorium. The air had been trapped in the auditorium for 2 days, and so was relatively pure at the start of the experiment. Section A of the graph was obtained when the instrument was filled with pure filtered air. Section B represents the change due to doubling the pressure of the filtered air. Section C was obtained by continually circulating the auditorium air through the instrument. The sharp rise from Section C was obtained by smoking a cigarette. The sharp rise from Section D to E represents another cigarette being smoked. Each cigarette (regular size, no filter) was smoked in about 3 min. and about 16 puffs were taken. Section F shows the gradual decay of the smoke. These results show that each cigarette, when the smoke was diluted to the 118,000 ft.^{3} of the auditorium, caused a scattering equal to 4 times the scattering of filtered air. Putting it another way: 1 cigarette causes light scattering equal to that of 500,000 ft.^{3} of filtered air. In this application the instrument was operated in an insensitized condition. For laboratory work the sensitivity can be increased by a factor of 100.

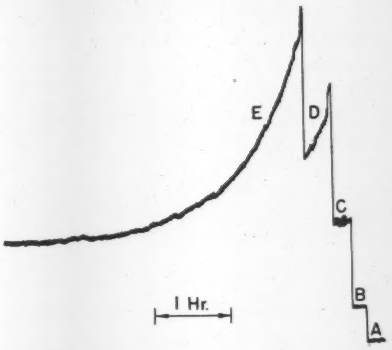

Fig. 4. Graph showing what happens to light scattering properties of auditorium air when 2 cigarettes are smoked in succession

A simple calculation will illustrate the contribution of this cigarette smoke to air pollution. The downtown portion of Pittsburgh, known as the Golden Triangle, contains about 50,000 people during the day. Since there is approximately enough air for each equal to the 118,000 ft.^{3} of the Mellon Institute auditorium (based on calculating the space consumed as being 500 ft. high and 1 mi. on each side of the Triangle), Fig. 4 could represent the outdoor air pollution resulting from the Triangle smokers having their first two cigarettes of the morning, supposing all of them to be smokers. If the full sensitivity of the instrument were utilized in this measurement, then 1 smoker in 1,000 could be detected.

The complexity of operation of this instrument has been decreased in comparison with an instrument previously built by the author. Further improvements are being made, and complete instrumental details will be presented in a later paper.

APCA
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(3) See footnote 3, page 212.

Concentration of Ozone in Cities

(continued from page 232)

investigated in the initial survey, nor in Washington, D. C., during the season when fogs are most likely to occur.

The levels of concentration of the oxides of nitrogen found in these observations bear no demonstrable relationship to the density of motor traffic. Relatively high concentrations of the oxides of nitrogen were observed at times, but their effect on the level of oxidant, as recorded instrumentally, could not be established with accuracy. This matter would seem to require further investigation.

The levels of concentration of carbon monoxide in the atmosphere, so far as this was investigated, appeared to vary with the density of motor traffic. The concentration during the day generally reached its peak during the period of maximum traffic, but on other days it remained at a uniform level (whether high or low) throughout the entire day. The latter fact would seem to indicate that there are highly significant sources of carbon monoxide in the atmosphere which do not depend upon vehicular traffic, or—what is more likely—that the concentration varies with the turbulence of the air at the site.

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Control of Atmospheric Pollution

(continued from page 211)

nants for specific conditions and threshold tolerance levels can be developed. Research in this field and studies by planning groups can develop useful criteria for eliminating the hazards of air pollution in critical areas. The smokeless zones created in selected industrial areas of England have demonstrated the feasibility of area planning(9). Industries in these zones are limited to the use of certain specific fuels. A benefit to adjoining neighborhoods is observed in the marked reductions in dustfalls and sulfur dioxide levels.

Conclusion

In conclusion it is appropriate to point out that only through science can the solutions to air pollution problems be found. Legal machinery and political action are necessary adjuncts but subordinate functions to be used in implementing the engineering decisions.

---

(9) *Smokeless Air, The Smoke Abatement Journal*, Quarterly, 1954.

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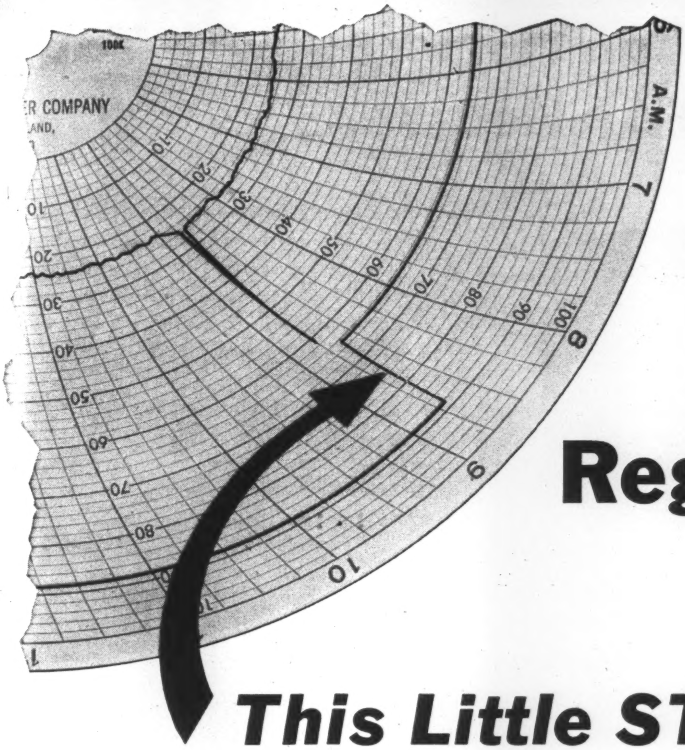

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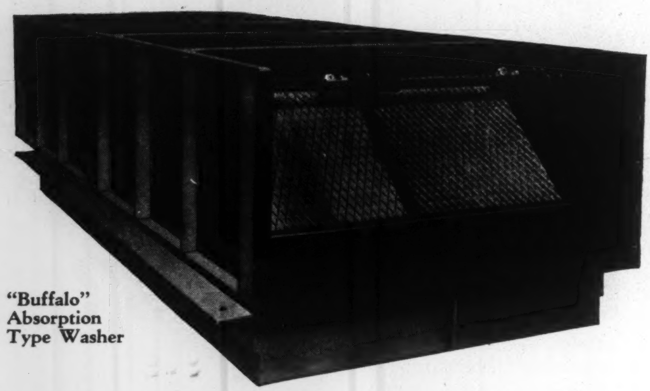

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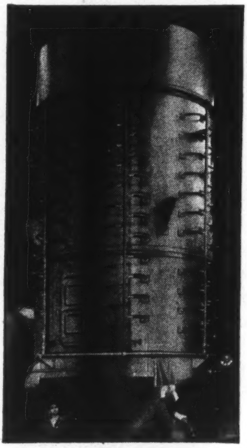

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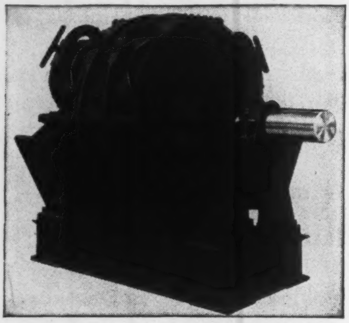

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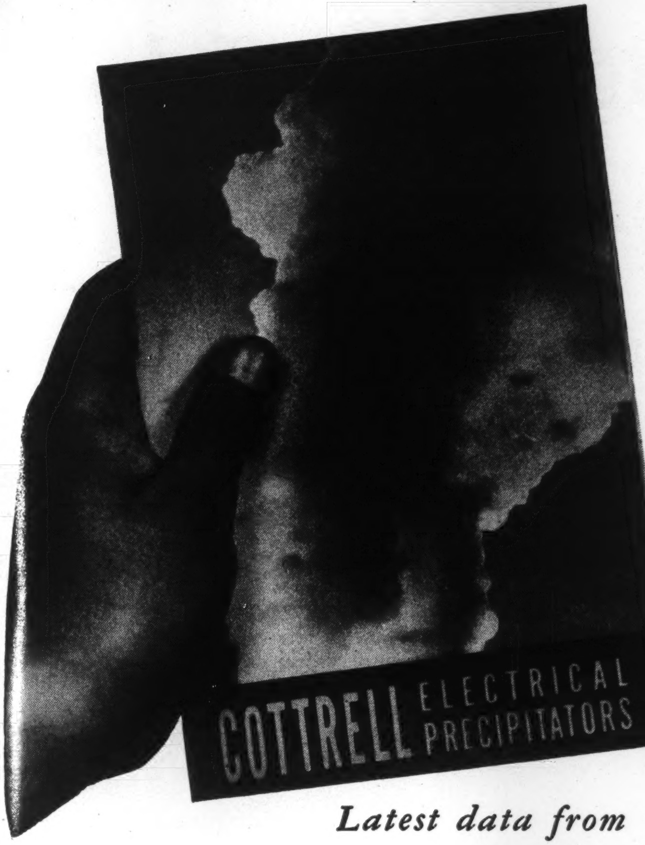

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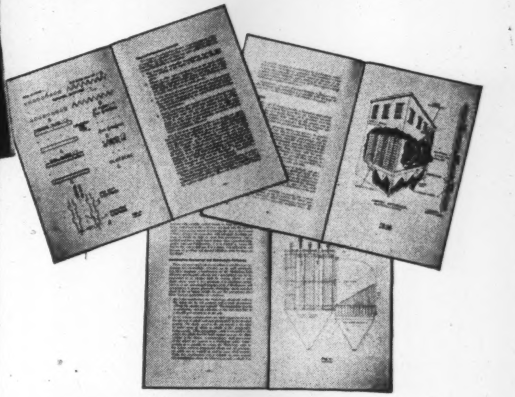

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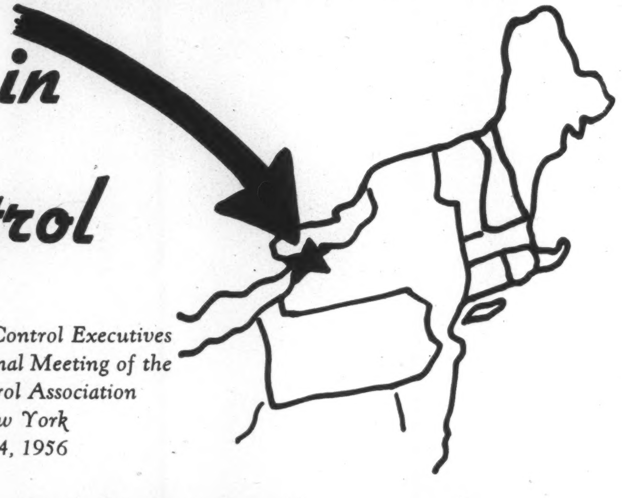

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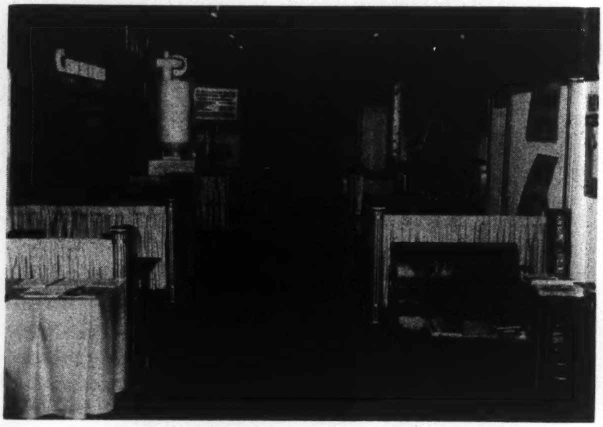

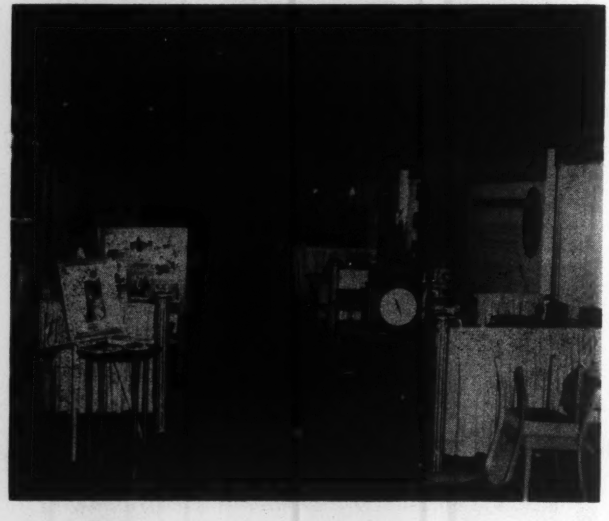

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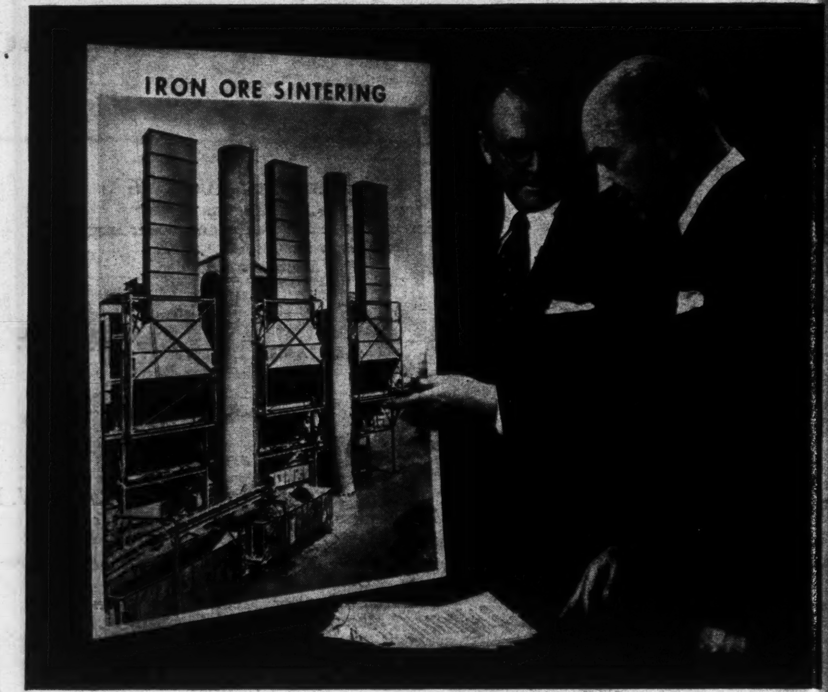
How the Steel Industry Is Fighting Air Pollution



When the public hears about dust and fume control it is often in terms of what has *not* been done. It is important that they should also know what *has* been done, because the record of the steel industry is one of the most progressive.

The purpose of this discussion is to give the executives the facts to prove this point.

Q. *First of all, how can you measure the progress of dust and fume control in the iron and steel industry?*

A. As you know, there are many ways to combat air pollution. Equipment and methods vary in effectiveness, but the industry agrees that electrical precipitators have the highest collection efficiencies. By keeping track of the demand for this high efficiency equipment over the years, we can get a good indication of the importance the industry places on dust and fume control and the progress they are making.

Q. *Do these figures show an increasing interest in this high efficiency equipment?*

A. Suppose we let the figures speak for themselves. Since 1945 precipitator capacity in the steel industry had a greater increase than in any previous ten year period. Precipitators handling about 6½ million cfm were installed during this period.

Q. *But can't you attribute this growth to the increase in steel-making capacity?*

A. Some of this growth is due to expanded production facilities, but that's just a part of it. For instance, iron and steel production has increased about 30% since 1945 — but precipitator capacity has increased about 130% during this same period.

Q. *In the old days, I guess precipitators were used primarily in blast furnaces, weren't they?*

A. That's right. The first one went into operation in 1930. Since then, 169 Research Cottrells have been ordered by the industry.

Q. *What about new applications?*

A. We have a number of new uses that have proven themselves on the job. Open hearths, for instance. In one installation, our precipitators reduced stack discharge to a little over 2 pounds per hour. That's quite a reduction when you consider that the discharge without a precipitator ranged from 75 to 245 pounds per hour.

Q. *I understand your Cottrells are used on some sintering machines now. Is this true?*

A. Yes, we have three in operation and more under construction.

Q. *How about scarfing machines?*

A. This is a recent application which has worked out very satisfactorily. Two precipitators are now in operation on this application.

Q. *Has anything been done on such problems as iron cupolas, electric furnaces, and ferromanganese blast furnaces?*

A. Yes. Installations have been made on all these problems.

Q. *How do you go about developing these new applications?*

A. We work very closely with our customers on these new projects. Our laboratory is a big help, and our 40 years of pilot plant experience plus over 2,000 precipitators give us the kind of experience that leads to the successful engineering of projects like these.

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